
Arnold Schwarzenegger
*Governor*

# DEVELOPING AND APPLYING PROCESS-BASED MODELS FOR ESTIMATING GREENHOUSE GAS AND AIR EMISSIONS FROM CALIFORNIA DAIRIES

PIER FINAL PROJECT REPORT

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# Preface

The California Energy Commission's Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

The PIER Program strives to conduct the most promising public interest energy research by partnering with RD&D entities, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following RD&D program areas:

- Buildings End-Use Energy Efficiency
- Energy Innovations Small Grants
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Transportation

What follows is the final report *Developing and Applying Process-Based Models for Estimating Greenhouse Gas and Air Emissions From California Dairies*, Contract #500-02-04, Work Authorization #MR-037 conducted by Applied Geosolutions, LLC, University of New Hampshire, University of California at Davis and University of California at Riverside. This project contributes to the PIER Program objectives of improving the environmental costs and risks of California's electricity.

For more information on the PIER Program, please visit the Energy Commission's Web site at: http://www.energy.ca.gov/research/ or contact the Energy Commission at 916-654-4878.

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# Abstract

In 2003, the National Academy of Sciences found that a commonly used method to estimate air emissions from feeding livestock in enclosed operations, such as feedlots, was inadequate and called for a new approach. While the former method involved calculating total emissions of an operation by using an emissions "average," the new recommended method uses a mathematical model to calculate the movement of substances of interest (for example, air emissions) during each stage of the process under consideration (for example, the production and consumption of dairy products). With support from the California Energy Commission's Public Interest Energy Research Program, the authors developed just such a process-based modeling tool to simulate greenhouse gas emissions from California dairies. The researchers performed a series of controlled chamber studies to measure greenhouse gases from dairy cows; developed a novel method for measuring nitrous oxide (a greenhouse gas) emissions from dairy corrals; created a process-based modeling tool (Manure-Denitrification-Decomposition) for estimating greenhouse gas emissions from dairies; and applied this tool with data collected regularly on soils, climate, and dairy locations to demonstrate the use of the tool for regional greenhouse gas emission inventories. Average methane emissions from enteric fermentation, which takes place in the digestive systems of the cows, were 108 and 160 kilograms methane per cow per year for dry and lactating cows, respectively. These are both considerable amounts of methane emissions per animal. Enteric fermentation also appears to be a source of nitrous oxide. Initial validation of the Manure-Denitrification-Decomposition model indicates that the model is well suited for assessing greenhouse gas emissions from animal feeding operations. However, additional validation is needed to quantify the uncertainties in model estimates.



**Keywords**: Biogeochemical modeling, dairies, Manure-DNDC, DNDC, methane, nitrous oxide, manure management, enteric fermentation, emission inventory, process-based modeling

# Executive Summary

## Introduction

In 2003, the National Academy of Sciences found that U.S. Environmental Protection Agency's current methods for estimating air emissions from feeding livestock were inadequate and called for a "process-based" approach, which uses a mathematical model to calculate the movement of substances of interest (for example, air emissions) during each stage of the process under consideration (for example, the production and consumption of dairy products). Applied Geosolutions, LLC, the University of New Hampshire, the University of California at Davis, and the University of California at Riverside conducted a study for the California Energy Commission to design and develop a just such a process-based model for estimating greenhouse gas emissions from California dairies. For this project, the team modified an existing model, called Denitrification-Decomposition, to simulate manure production, manure dynamics, trace gas emissions, crop growth, and soil carbon dynamics under various dairy management systems in California. This new model is called Manure-Denitrification-Decomposition.

## Purpose

This study estimated greenhouse gases emissions from dairies and measured greenhouse gases emissions from dairy cows, including nitrous oxide emissions. The data collected is used for regional greenhouse gas emission inventories.

## Project Outcomes

There are approximately 1.7 million milking dairy cows in California. Emission inventories list dairy cows and their manure as the major source of regional air pollutants, but data on their actual emissions remain sparse, particularly for smog-forming volatile organic compounds and greenhouse gases. The authors report measurements of methane and nitrous oxide emitted from non-lactating (dry) and lactating dairy cows and their manure under controlled conditions. The experiments were conducted in an environmental chamber that simulates commercial concrete-floored freestall cow housing conditions.

## Conclusions and Recommendations

The Manure-Denitrification-Decomposition model was designed and implemented through field measurements, information/data collection, algorithm development and code integration. Early tests proved the model was able to handle the complex calculations of mass movements and biogeochemical dynamics among different stages of animal feeding operations. However, for a complex, process-based model such as Manure-Denitrification-Decomposition, setting up of a framework is only the first step of the model development. Calibration and validation with the data observed at each of the stages of manure production and decomposition are crucial to make the model reliable and to develop a strong statistic understanding of model uncertainty. Initial validating results are encouraging and indicate that the Manure-Denitrification-

Decomposition model is a promising tool for compiling emission inventories from California dairies. Unfortunately, so far, this research has obtained only a limited amount of field data to complete this unavoidable stage of the model development.

**Benefits to California**

In summary, this project achieved its main goals of designing and building a process-based modeling tool for estimating greenhouse gas emissions from individual dairies or regions with dairies and building spatial databases. The Manure-Denitrification-Decomposition model will become useful for building emission inventories for California dairies and for assessing opportunities for reducing net greenhouse gas emissions at farms. Further work is needed to perform more extensive model validation to improve understanding of the accuracy and uncertainties of model estimates. The authors recommend the following steps:

- Collect additional greenhouse gas emission data specifically for model validation. Data should be collected using automated chambers (to capture the incidental nature of nitrous oxide emissions). Chamber data can be used to assess the usefulness of a particular type of lab equipment that uses infrared technology to estimate emissions.
- Perform additional studies on nitrous oxide emissions directly from dairy cows, including testing various feeding routines.

# 1.0 Technical Summary

## 1.1. Introduction

While the Denitrification-Decomposition biogeochemical model has been used and tested extensively across a wide range of cropping, climate, and soil conditions, this is the first time it has been used specifically for animal feeding operations. A virtual farm was constructed in the Manure- Denitrification-Decomposition model (Manure-DNDC) to generalize or represent a wide range of animal farms in California or other parts of the world. The virtual farm consists of seven components namely housing, outdoor corrals, grazing plot, lagoon, compost, digester and field where the manure is produced, stored, treated or applied, respectively. These components are integrated into a processing entity that tracks the entire manure life cycle. The Manure-DNDC model runs at a daily or hourly time step. Daily fluxes of ammonia, methane, nitrous oxide, and carbon dioxide as well nitrate leaching are calculated for each of the seven farm components. The sum of the fluxes from all seven components constitutes the farm emissions.

### *1.1.1. Projected Outcomes*

The fluxes of nitrous oxide and methane were measured from cows and/or their fresh manure. Average estimated methane emissions were predominately associated with enteric fermentation from cows rather than manure and were 108 and 160 kilograms methane per cow per year (kg $CH_4$ $cow^{-1}$ $yr^{-1}$) for dry and lactating cows, respectively. Lactating cows produced considerably more $CH_4$ emissions than dry cows. Elevated nitrous oxide emissions were measured with cows in the chamber indicating direct emissions likely from enteric fermentation. Average direct nitrous oxide emissions from cow enteric fermentation were equivalent to approximately 1 kilogram nitrous oxide per cow per year (kg $N_2O$ /cow/year). This enteric source of nitrous oxide emission is potentially an important new finding that calls for additional research for further quantification. In summary, dairy cows and fresh manure have the potential to emit considerable amounts methane.

In a separate analysis, a total of 96 pregnant, non-lactating Holstein cows were housed in four, totally enclosed cattle pen enclosures and were fed a total mixed ration *ad libitum*. Eight cows were housed in each of the four enclosed cattle pen during each of three, 14 day replications. Cows were randomly sorted into four groups and stratified by weight. Treatments were: (1) control, manure accumulated for 14 days, (2) harrowing, three times weekly, (3) surface acidifier application, twice weekly, and (4) scraping, which was complete manure removal once weekly. Emissions of greenhouse gases, carbon dioxide, nitrous oxide, and methane were measured continuously from the cattle pen enclosure air inlets and outlets. Gaseous concentrations were sampled using a photoacoustic gas-analyzer (INNOVA 1412) and emission rates kilograms methane per cow per year (kg/cow/yr) calculated. Data were analyzed using Proc MIXED procedures in surface acidifier application. Scraping compared to surface acidifier application, harrowing, and control showed reduced emission rates for nitrous oxide and methane. Emission rates for methane and nitrous oxide were higher in surface acidifier

application compared to the other treatments. Results suggest that surface acidifier application increases greenhouse gases.

A third measurement study collected ambient concentrations of nitrous oxide at 4 separate elevations, one, two, five, and 10 meters above a dairy dry lot at California State University Fresno. This data was collected using a Fourier Transform InfraRed Spectroscopy system with a 10 meter sampling tower which was also configured to collect corresponding meteorological data. The data was then used to make approximate estimations of nitrous oxide flux using the flux gradient method. Ambient nitrous oxide concentrations were observed to be elevated just after a rain event, typically by around 10 percent. These measurements indicate annualized fluxes ranging from 1.96 to 4.33 kilograms nitrous oxide per hectare per year (kg $N_2O$/ha/yr). Ideally a longer term continuous monitoring of nitrous oxide in an open path format would be able to better define annual variability, lead to less variable calculations in the emission rates and factors, and provide data more suitable for validating process models.

### *1.1.2. Conclusions and Recommendations*

A suite of spatially explicit geographic information systems data for soils, climate, dairy locations, dairy cow populations, and dairy management was developed and assembled to define the biophysical characteristics for driving the Manure - DNDC model. Spatial databases of climate using the California Irrigation Management Information System (CIMIS), soils using the Natural Resource and Conservation Service soil survey's (NRCS), dairy location (from Department of Water Resources land use maps) and manure management practices (derived from Air District Dairy permits) were used to create input files for Manure - DNDC. The project used 2004 statistics and climate data to estimate methane and nitrous oxide emissions from all dairies in California. Modeled total methane emissions for 2004 were 9.8 million metric tons carbon dioxide equivalence (MMT $CO_2$ eq). Total nitrous oxide emissions from cows themselves (enteric), manure management and land application of manure were 0.8 million metric tons carbon dioxide equivalence, 2.0 million metric tons carbon dioxide equivalence and 6.9 million metric tons carbon dioxide equivalence, respectively.

### *1.1.3. Benefits to California*

The Manure-DNDC models capacity can be applied for quantifying whole farm emissions from California Dairies. This project will extend Manure-DNDC applications by integrating the fundamental biogeochemical processes with animal housing and manure management practices for better model representation in California. The new version of DNDC includes features to analyze the fate of manure through the incorporation of dairy specific management conditions and local climatological and soil conditions and may ameliorate ambiguities previously estimated. The process-based model estimates of methane emissions are comparable to the 2004 California Energy Commission's emission inventory estimates of 10.4 million metric tons carbon dioxide equivalence but the model's estimate of nitrous oxide from manure management is approximately one third of the California Energy Commission's 2004 estimate.

# 2.0 Introduction

## 2.1. Background and Overview

In 2003, the National Research Council (NRC 2003) found that the U.S. Environmental Protection Agency's (EPA) current methodologies for estimating air emissions are inadequate and called for "process-based" modeling instead of an "emission factor" approach. The measurement and monitoring of dairy-related air emissions and emission reductions is complex because the emission sources are dispersed and largely driven by biological activity with significant variability over time, space, and management practices. Emissions are further affected by local and regional meteorological conditions. This complexity results from the interaction of a suite of biogeochemical processes such as decomposition, nitrification, denitrification, fermentation, and ammonia volatilization. This project will modify an innovative, internationally recognized "process-based" model called the Denitrification-Decomposition (DNDC) model, which already contains these biogeochemical processes, to create a scientifically sound tool for significantly improved estimates of emissions from California dairies.

### *2.1.1. Greenhouse Gas Emissions From California Dairies*

Twenty-one percent of the nation's milk supply comes from California, making it the leading dairy state in the United States (California Agricultural Resource Directory, 2005). There is concern that the large number of dairy cows (approximately 1.8 million dairy cows and 0.7 million associated heifers) impacts environmental quality. The San Joaquin Valley of California is the leading dairy region of the United States but also known as the worst non-attainment area for smog. Cows, feed, and waste are sources of volatile organic compounds (VOCs), which are major contributors to tropospheric ozone (smog), and also greenhouse gases, which increase global warming.

Sources of greenhouse gases from dairies include cows (enteric fermentation occurring in the rumen), manure in animal housing and outdoor storage, treatment of manure and slurry (e.g., composting and anaerobic treatment), land application, and chemical fertilizers (Monteny *et al.*, 2001).

On most California dairies, waste management techniques differ between the concrete floored freestall barns where lactating cows are housed and the dirt floored corrals where dry cows and heifers are typically housed. Manure that collects in freestall barns is flushed or scraped several times daily, and the resulting waste stream is stored in large manure ponds (lagoons). Manure from open dirt corrals is typically scraped to storage piles several times a year. Complete and frequent removal of waste in drylot corrals, using techniques such as scraping, may be an effective mitigation strategy for reducing greenhouse gases (GHGs) in the immediate area (Monteny *et al.*, 2001, Weiske *et al.*, 2006). However, GHG emissions may increase in the manure storage areas (Weiske *et al.*, 2006).

Although most $CH_4$ and $CO_2$ are released from the animals, some of these gaseous emissions, as well as emissions of $N_2O$, also result from microbial processes in the excreta or after manure is

land applied (Clemens and Ahlgrimm, 2001). Therefore, it is important to also consider the management of waste when determining appropriate mitigation strategies for greenhouse gases from dairies. The growth of microbes in fresh waste may be impaired by environmental factors such as pH, temperature, and oxygenation of the waste. Therefore, it is important to address at least one of the main factors (e.g., pH) to effectively disrupt the microbial and enzymatic activity in order to reduce the gaseous emissions released into the atmosphere (Jongebreur and Monteny, 2001). Adding oxygen to the slurry to prevent the anaerobic activity responsible for much of the gaseous emissions can be achieved by frequently raking (aka harrowing) the waste with a chain harrow. Since growth and activity of rumen bacteria are inhibited at low pH (Stewart, 1977, Russell and Dombrowski, 1980, Thurston *et al.*, 1993), application of acidifying agents may also reduce the gaseous emissions from fresh waste.

When considering an acid to use for pH reduction in dairy slurry, it is important to consider the compatibility of the acid with the presence of animals. Sodium bisulfate (SBS) is a dry, granular acid salt that has been used for many years as a pH reducer in a variety of agricultural, industrial, and food applications. The anti-bacterial properties of SBS have been exploited in its application as a sanitizer (EPA Reg #1913-24-AA). Sodium bisulfate has been used for bacterial reduction in poultry, dairy, and equine waste and bedding due to its pH reducing and antimicrobial properties, and has been found to significantly decrease ammonia emissions in these facilities (Sweeney *et al.*, 1996, Ullman *et al.*, 2004). Research is needed to determine the effects of SBS on GHG emissions from dairies.

### *2.1.2. Need for Process-Based Biogeochemical Models*

Accurate assessment of air emissions from dairies with emission factors is difficult due to: (1) high variability in the quality and quantity of animal waste, and (2) the numerous factors affecting the biogeochemical transformations of manure during collection, storage and field application. Measurement programs are essential but expensive and thus have not been extensively implemented. Therefore, process-based models that incorporate mass balance constraints are needed to extrapolate air emissions in both space and time (NRC, 2003). EPA has not yet developed such a model, relying instead on a simplified methodology for estimating air emissions from individual dairies, using "model" farms based on typical animal confinement, manure collection, solid separation, manure storage and stabilization, and techniques for land application of manure (EPA 2002).

Although it is well known that constant emission factors are not effective for quantifying GHG, ammonia, and reactive organic gas (ROG) emissions from concentrated animal feeding operations (CAFOs) (NRC 2003), managers and regulators generally lack access to tools that are both scientifically sound, capture the biogeochemical processes that impact emissions, and are relatively easy to use. There are a number of advantages to developing process-based models of element transformations and emissions from the *combined* components (animal feedlot, manure storage and handling, land application of manure) of dairies:

- Dynamic, process-based models, developed from laboratory and field studies, **do not rely on constant emission factors**. They assess the impact on emission factors of

varying conditions (e.g., climate, storage facility, soils). These models will continue to improve as more field studies are conducted and published, and they do not obviate the need for a strong measurement program.

- By **enforcing a mass balance** in the model (i.e., conservation of mass), the sum of all emission factors are constrained to be ≤ 100% of inputs. This is both good bookkeeping and essential for evaluating trade-offs in mitigation strategies.
- Full system analysis with dynamic, process-based models can inexpensively and efficiently **evaluate mitigation scenarios** under various conditions, and can help target mitigation toward facility component(s) and/or operation(s) that cause the greatest emissions.
- Simultaneously provide estimates of all emission for **comprehensive assessments** of mitigation efforts. For example, *efforts to reduce methane may result in increased nitrous oxide emissions that could more than offset gains from methane reductions and result in a net increase in total greenhouse gas emissions*. Therefore, ***well validated models are critical for comprehensive analyses that capture all emissions to air and water***.

### 2.1.3. Background on DNDC Model and Capabilities

During the past decade, multi-agency support from EPA, National Aeronautics and Space Administration (NASA), and National Science Foundation (NSF) has guided the development, testing, and application of a research biogeochemical model of nitrogen (N) and carbon (C) cycling in soils. The process-oriented computer simulation model, Denitrification-Decomposition (DNDC), was developed based on the biogeochemical concepts for predicting soil biogeochemistry (Li et al. 1992, 1994, 1996; Li 2000). The first component, consisting of the soil climate, crop growth and decomposition sub-models, predicts soil temperature, moisture, pH, redox potential (Eh) and substrate concentration profiles (e.g. ammonium, nitrate, dissolved organic carbon) based on ecological drivers (e.g., climate, soil, vegetation and anthropogenic activity). The second component, consisting of the nitrification, denitrification and fermentation sub-models, predicts nitric oxide (NO), nitrous oxide ($N_2O$), methane ($CH_4$) and ammonia ($NH_3$) fluxes based on the environmental variables in the soil. Classical laws of physics, chemistry and biology, and empirical equations generated from laboratory observations, were used in the model to parameterize each specific reaction. The entire model forms a bridge between basic ecological drivers including management of agro-ecological systems, and water, carbon, and nitrogen cycles. DNDC utilizes geographic information system (GIS) databases with spatially and temporally differentiated information on climate, soil, vegetation and farming practices for local, regional and national scale analyses.

The core of DNDC is a soil biogeochemical model, which can be linked to vegetation models to predict carbon sequestration and nitrogen cycling for different ecosystems. DNDC has been linked to a crop model (Zhang et al. 2002) to simulate soil organic carbon (SOC) dynamics and emissions of dinitrogen ($N_2$) and several trace gases including $N_2O$, nitrogen oxide (NO), ammonia ($NH_3$) and methane ($CH_4$) from both upland and wetland agricultural ecosystems. DNDC is a unique process-based biogeochemical model because it (1) simulates both aerobic and anaerobic conditions, (2) tracks eH, (3) can provide a comprehensive simulation of nutrient

releases to air and water, including emissions of ammonia, greenhouse gases and nitrate leaching, and (4) contains tools for examining sensitivity and uncertainties in emission estimates. These capabilities are critical for quantifying whole farm emissions from California dairies. This model has been independently tested and validated by many researchers and under a wide range of conditions worldwide and now is utilized for national trace gas inventory studies in the U.S., Canada, the United Kingdom, Germany, Italy, New Zealand, China, Japan, Thailand, and the Philippines. The extensive validation and applications worldwide indicate that the fundamental processes embedded in DNDC have provided a sound basis for modeling C and N dynamics across a broad range of climatic zones, soil types and management regimes.

## 2.2. Project Objectives

The project goal is to modify the DNDC model to create a tool for simulating C and N biogeochemical cycling in a dairy operation, tracking the manure life cycle (production, storage/processing, field application) and determining the fate of manure C and N (volatilized, incorporated into soils or vegetation, lost via leaching) for California dairies. This project will extend DNDC applications by integrating the fundamental biogeochemical processes with animal housing and manure management practices. The new model elements include: (1) integration of detailed biogeochemical processes under animal housing and manure storage conditions; (2) characterization of environmental factors under housing or storage conditions; and (3) characterization of quantity and quality of animal waste at each dairy. The new version of DNDC includes features to analyze the fate of manure through the incorporation of dairy specific management conditions and local climatological and soil conditions. The resulting tool can be used to provide improved estimates of releases of C and N to air (e.g. $CH_4$, NO, $N_2O$, $NH_3$,) and water (nitrate leaching from field application phase).

Specific objectives of the project include the following:

- Enhance the DNDC model creating a new tool (Manure-DNDC) for simulating carbon and nitrogen biochemical cycling in dairy operations, tracking the manure life cycle (volatilized, incorporated into soils or vegetation, lost via leaching) for California dairies.
- Complement existing measurement programs to include $N_2O$ measurements.
- Use laboratory data to be collected by University of California, Davis (UC Davis) to generate improved understanding of air emissions from dairy cows and drylot conditions.
- Develop a Fourier transform infrared spectroscopy (FTIR) system at University of California, Riverside (UC Riverside) for measuring $N_2O$ emissions from drylot conditions.
- Use laboratory and field data to validate the Manure-DNDC model.
- Develop the GIS Databases and tools that can be used to collect input data necessary for estimating GHG emissions from dairies operations in California.

## 2.3. Report Organization

Final report presents major components of the research project as separate chapters in the report. Two appendices are provided. Appendix A provides details of the biogeochemical processes in Manure-DNDC. Appendix B provides details on the design and testing of the FTIR systems developed for measuring $N_2O$ emissions from drylots.

# 3.0 Approach

## 3.1. Developing Manure-DNDC Model

From the biogeochemical view, animal manure is nothing but a complex of organic compounds plus minor inorganic components. As soon as fresh manure is produced from the anaerobic enteric systems of the livestock, the manure solids will immediately be exposed to the aerobic conditions and start decomposing. During the decomposition, which occurs due to microorganisms in the manure, a fraction of the organic matter will be transformed into inorganic C (e.g., $CO_2$) or N (e.g., ammonium or $NH_4+$). Meanwhile the urea contained in the liquid fraction of the animal waste will undergo hydrolysis, which converts urea into $NH_4+$. Controlled by thermodynamic equilibrium, $NH_4+$ is then converted to ammonia ($NH_3$) in the liquid phase of manure. Due to substrate concentration gradients, the $NH_3$ will diffuse to the air-water interface in the manure, and be partially emitted into the air. Nitrifying bacteria in the manure will oxidize $NH_4+$ into nitrate ($NO_3-$). $NO_3-$ can subsequently be converted into nitrous oxide ($N_2O$), nitric oxide (NO) and dinitrogen ($N_2$) through denitrification. NO3- can also be leached from the manure. A process-oriented computer simulation model, Manure-DNDC, was developed to integrate these biogeochemical processes into a computational framework for quantifying environmental impacts of management practices for dairy farms in the California. The model was built up upon an existing model, Denitrification-Decomposition or DNDC. The core of DNDC is a process-based computer simulation model of soil biogeochemistry which predicts transport and transformation of C and N in soil profiles driven by a series on biochemical or geochemical processes. The biogeochemical processes are decomposition, urea hydrolysis, ammonium-ammonia equilibrium, ammonia volatilization, nitrification, denitrification, nitrate leaching and fermentation. The fluxes of C or N gases such as $CO_2$, $CH_4$, $NH_3$, $N_2O$, NO and $N_2$ are calculated by the model as final, intermediate or byproducts of the biogeochemical processes. During the past 18+ years, DNDC's biogeochemical processes have been calibrated and validated against field observations across a wide range of terrestrial soils worldwide. By linking the core of DNDC to vegetation models of crop, grassland or forest, DNDC has been successfully applied for estimating plant production, soil C sequestration and trace gas emissions across the major terrestrial ecosystems. Manure-DNDC was constructed by linking the biogeochemical processes that form the core of DNDC to a virtual animal farm.

### *3.1.1. Construction of a Virtual Farm*

Animal farms affect environmental quality by releasing gaseous, liquid or particulate matter that is potentially harmful to the environment. The harmful matter such as ammonia (NH3), methane ($CH_4$), nitrous oxide ($N_2O$), volatilized organic carbon (VOC), dusts etc. can be produced from either the animal metabolic processes or the animal waste (manure) transport or transformations. In California, the manure life cycle usually spans three main phases of manure management including feeding lot, storage/treatment and field application; and each of the phases could occur in several types of systems. For example, the feeding lot systems include enclosed housing (e.g. freestalls), outdoor pen (e.g. drylot) or grazing field; the storage/ treatment systems include compost, lagoon or anaerobic digester; and the field application phase includes application to fields with different crops or varied farming management

practices. A virtual farm was constructed in Manure-DNDC to generalize and represent a wide range of dairy farms in California by including the major components, namely house, outdoor pen, grazing lots, lagoon, compost, digester and field application (Figure 1).

The components house, outdoor pen and grazing plot are where the animals are fed and rest. In Manure-DNDC, the feeding lot components play three roles in (1) defining fresh manure production; (2) regulating transport and transformation of the manure accumulated in the feeding lots; and (3) determining enteric gas production. As such, the model requires input information about the characteristics of the herd and feeding lots condition. The herd characteristics include animal types, population, and feed quantity and quality (e.g. crude protein contents). The feeding lot characteristics include floor area, ground surface property, bedding material and frequency, ventilation and manure removal method. Driven by the herd and lot characteristics as well the daily weather data, Manure-DNDC tracks the dynamics of temperature, moisture, pH, redox potential (Eh) and substrates concentration in the manure stored in the feeding lots to predict the biogeochemical processes (e.g., decomposition, ammonia volatilization, nitrification, denitrification and fermentation) occurring in this initial phase of manure management.

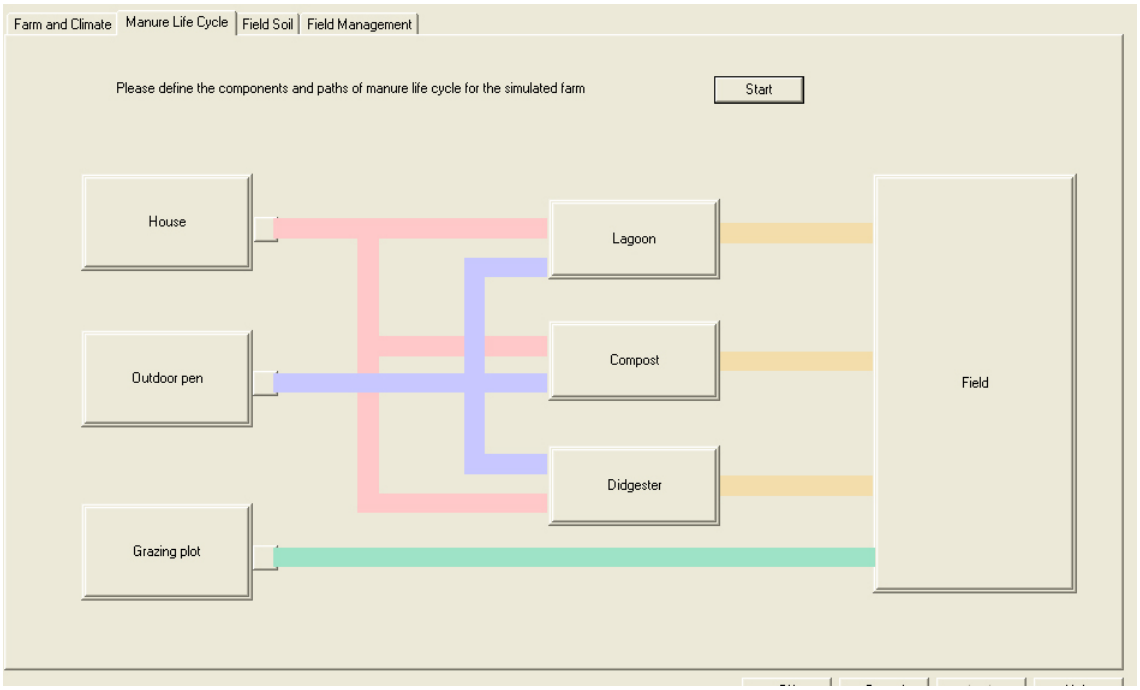


**Figure 1. A virtual farm built in Manure-DNDC to generalize a wide-range of animal farms in the U.S. The virtual farm consists of seven components which are linked to each other through the manure life cycle.**

The model can simulate the collection of manure solids from the feeding lots that are composted. Manure-DNDC tracks the manure accumulation in and removal from the compost as well as changes in environmental conditions of the compost, including temperature, moisture, oxygen consumption, redox potential (Eh) and substrates concentration. These modeled environmental factors are used to drive the biogeochemical processes of aerobic decomposition, ammonia volatilization, nitrification, denitrification and fermentation occurring in the compost. Users must specify the characteristics of the composting system, including the compost density and size, additives, storage duration, and aeration practices.

The lagoon component of the virtual farm receives the manure liquids collected from the feeding lots (e.g. after solid separatation. Manure-DNDC simulates the temperature, pH, Eh and substrates concentration in the lagoon slurry based on the weather data, lagoon capacity and surface coverage. The biogeochemical processes (e.g., anaerobic decomposition, gas exchange between liquid and gas phases, ammonia volatilization, nitrification, denitrification and fermentation) are modeled based on slurry quantity and quality in conjunction with the modeled environmental factors in the lagoon.

In Manure-DNDC, the anaerobic digester component is defined by the digester's capacity, CH4 productivity, additives, treatment temperature and duration. Based on a mass balance calculation, the residue slurry from the digester is defined by its organic C content and C/N ratio.

The model also simulates the fate of manure from the compost, the lagoon or the digester storage and treatment components once it is applied to fields on the farm. If the manure is applied to the farm's land, the field's soil properties, crop cultivation and other farming management practices (e.g., tillage, irrigation, fertilization, flooding, grass cutting etc.) will be required as input information. As soon as the manure is applied in the soil, the manure will be partitioned into the soil organic matter (SOM) pools based on the quantity and quality (i.e., C/N ratio) of the manure. Manure-DNDC simulates the biogeochemical processes of SOM and quantifies their contributions to $CO_2$, $CH_4$, $NH_3$ and $N_2O$ emissions to the atmosphere.

The components described above have been integrated in the model for mass balance tracking the manure life cycle across the complete manure management system (Figure 2). Table 1 provides a list of required input parameters required by the model, the biogeochemical processes embedded in the model, and the model output parameters. Since a farm may not contain all the components, users can select which of the components to simulate through the model input interface to compile a virtual farm to match individual farm characteristics.

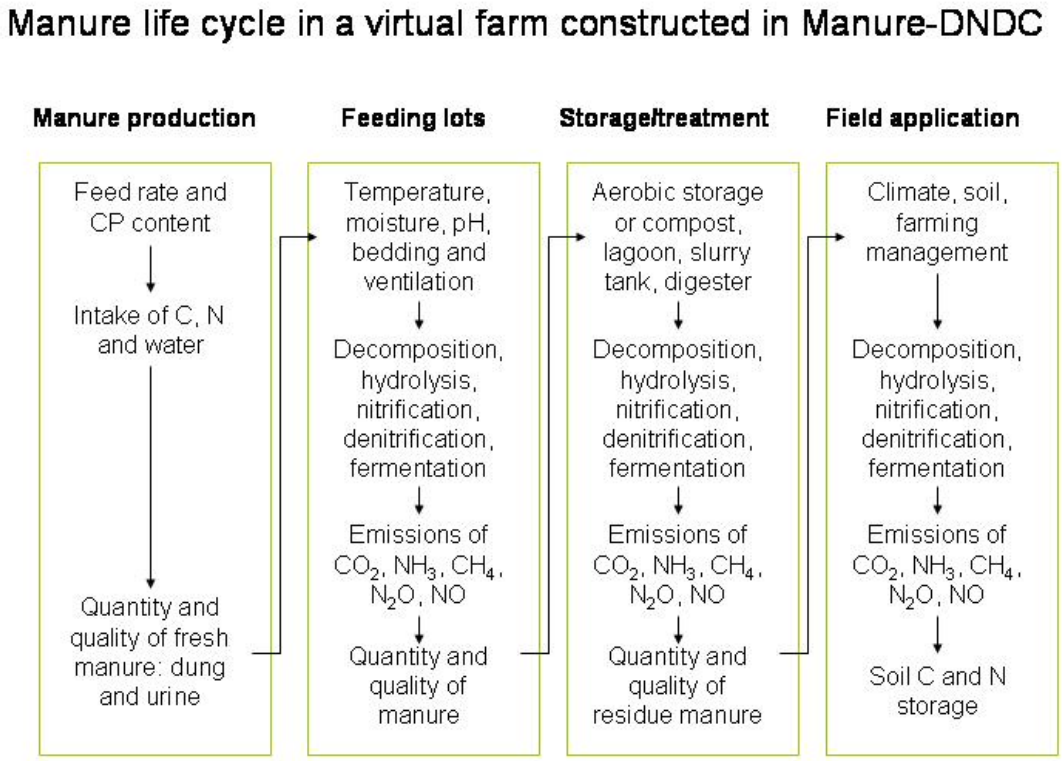


**Figure 2. Manure life cycle across the farm components in Manure-DNDC**

**Table 1. Input/output parameters and modeled processes for manure management components of the virtual farm built in Manure-DNDC**

| Farm component | Input parameters | Modeled processes | Output parameters |
|---|---|---|---|
| House | Air temperature;<br>Wind speed;<br>Animal type and heads;<br>Feed rate;<br>Crude protein content;<br>Floor area;<br>Floor surface properties;<br>Bedding material type, amount, C/N ratio and timing;<br>Ventilation type and rate;<br>Frequency and method of animal wastes removal;<br>Fractions of animal wastes partitioned to compost, lagoon, digester and remaining in house. | Indoor temperature and air flow rate;<br>Conversion of feeding materials to productions of milk, meat, urine and feces;<br>Manure accumulation on floor or in gutter;<br>Manure temperature, moisture, pH and Eh dynamics;<br>Biogeochemical processes* in manure. | Quantity and quality (C/N ratio) of manure released from house;<br>Partitioning of liquid and solid manure to compost, lagoon and/or digester;<br>Enteric $CH_4$ and $N_2O$ fluxes;<br>Fluxes of $NH_3$, $CH_4$, $N_2O$, NO, $N_2$, $CO_2$ emitted from floor or gutter. |

| | | | |
|---|---|---|---|
| Outdoor pen | Air temperature;<br>Precipitation;<br>Wind speed;<br>Animal type and heads;<br>Feed rate;<br>Crude protein content;<br>Ground area;<br>Ground surface properties;<br>Bedding material type, amount, C/N ratio and timing;<br>Frequency and method of animal wastes removal;<br>Fractions of animal wastes partitioned to compost, lagoon, digester and remaining in pen. | Conversion of feeding materials to productions of milk, meat, urine and feces;<br>Manure accumulation on ground;<br>Manure temperature, moisture, pH and Eh dynamics driven by weather data;<br>Biogeochemical processes* in manure. | Quantity and quality (C/N ratio) of manure released from outdoor pen;<br>Partitioning of liquid and solid manure to compost, lagoon and/or digester;<br>Enteric $CH_4$ and $N_2O$ fluxes;<br>Fluxes of $NH_3$, $CH_4$, $N_2O$, NO, $N_2$ and $CO_2$ emitted from ground. |
| Grazing plot | Field area for grazing;<br>Grazing application periods;<br>Start and end dates for each grazing period;<br>Hours per day for the animals stay in the grazing field;<br>Animal type and heads;<br>Frequency and method of animal wastes removal;<br>Fractions of animal wastes partitioned to compost, lagoon, digester and remaining in the field. | Production of urine and feces driven by grass quantity and quality available in the field;<br>Manure accumulation on and incorporation in soil;<br>Biogeochemical processes* in manure;<br>Nitrate leaching. | Quantity and quality (C/N ratio) of manure removed from field;<br>Partitioning of removed manure to compost, lagoon and/or digester;<br>Enteric $CH_4$ and $N_2O$ fluxes;<br>Fluxes of $NH_3$, $CH_4$, $N_2O$, NO, $N_2$ and $CO_2$ emitted from manure accumulated on soil;<br>Nitrate leached to soil. |
| Aerobic compost | Quantity and quality (C/N ratio) of manure received from house, outdoor pen and/or grazing plot;<br>Compost storage size and density;<br>Storage duration;<br>Additional litter amount and C/N ratio;<br>Fractions of mature compost partitioned to field application, market selling and remaining in compost. | Temperature, moisture, pH and Eh dynamics within compost;<br>Biogeochemical processes* in compost. | Quantity and quality (C/N ratio) of manure removed from compost;<br>Partitioning of removed manure to field application;<br>Fluxes of $NH_3$, $CH_4$, $N_2O$, NO, $N_2$ and $CO_2$ produced during composting. |

| | | | |
|---|---|---|---|
| Anaerobic lagoon or tank | Quantity and quality (C/N ratio) of manure received from house, outdoor pen and/or grazing plot;<br>Capacity;<br>Surface area;<br>Surface coverage;<br>Rain water intake;<br>Slurry drain frequency;<br>Fractions of slurry partitioned to field application, market selling and remaining in lagoon. | Temperature, moisture, pH and Eh dynamics in lagoon or tank;<br>Biogeochemical processes* in lagoon or tank. | Quantity and quality (C/N ratio) of slurry removed from lagoon or tank;<br>Partitioning of removed slurry to field application;<br>Fluxes of $NH_3$, $CH_4$, $N_2O$, NO, $N_2$ and $CO_2$ emitted from lagoon or tank. |
| Anaerobic digester | Quantity and quality (C/N ratio) of manure received from house, outdoor pen and/or grazing plot;<br>Digester capacity;<br>Methane production;<br>Processing temperature;<br>Processing duration;<br>Fractions of digester residue partitioned to field application, market selling and remaining in digester. | Temperature, moisture, pH and Eh dynamics in anaerobic digester;<br>Biogeochemical processes* in digester. | Quantity and quality (C/N ratio) of digested residue removed from digester;<br>Partitioning of removed residue to field application;<br>Fluxes of $CH_4$ and CO2 produced in digester. |
| Field | Quantity and quality (C/N ratio) of manure received from compost, lagoon and/or digester;<br>Soil properties;<br>Cropping management practices: crop type and rotation, tillage, fertilization, manure application timing and method, flooding and drainage, irrigation and grass cutting. | Crop growth;<br>Soil climate;<br>Applications of cropping management practices including manure/slurry amendment;<br>Soil water hydrology;<br>Biogeochemical processes* in soil. | Fluxes of $NH_3$, $CH_4$, $N_2O$, NO, $N_2$ and $CO_2$ emitted from soil;<br>Soil carbon sequestration;<br>Nitrate leaching;<br>Crop yield. |

* Biogeochemical processes include decomposition, hydrolysis, nitrification, ammonia volatilization, denitrification and fermentation.

### *3.1.2. Integration of Farm Components Based on Biogeochemical Concepts*

Manure-DNDC was developed based on the scientific concepts of biogeochemistry, which include biogeochemical abundance, field, coupling and cycling (Li, 2007). Biogeochemical field

is the assemblage of environmental forces or factors, including gravity, radiation, temperature, moisture, pH, Eh, and substrate concentration gradients. These factors construct a multi-dimensional field in which the transport and transformation of chemical elements occur. The biogeochemical field plays a key role in integrating various factors and processes into an entirety such as a farm ecosystem. A biogeochemical field is produced by primary drivers (e.g., climate, soil, topography, vegetation, and management activity) in a specific ecosystem, and it determines all of the relevant biochemical or geochemical processes and hence the ecosystem evolution. Mathematically expressing the biogeochemical field is a key step to predicting the transport and transformation of chemical elements in ecosystems. Biogeochemical modeling reconstructs the dynamics of the biogeochemical fields as they continually vary in space and time. For example, in a dairy farm, the transformations of C or N in the manure are realized through a series of biochemical or geochemical reactions including mechanical movement, dissolution/crystallization, decomposition/combination, oxidation/reduction, adsorption/desorption, complexation/decomplexation, and assimilation/dissimilation. As do all chemical reactions, each of the processes has two directions to lead to elemental coupling or decoupling in various forms. The direction and rate of each reaction is usually controlled by more than one environmental factor. Elemental coupling and decoupling through the biochemical or geochemical reactions are driven by both internal factors (e.g., atomic structure, bond energies, electronegativies etc.) and external factors (e.g., gravity, radiation, temperature, moisture, pH, Eh, substrate concentration gradients etc.) forming the biogeochemical field. A myriad of coupling/decoupling phenomena shape the complexity of an element's biogeochemical cycle. Theoretical analyses of thermodynamics, chemical reaction kinetics, bond energy/enthalpy, and quantum chemistry have been used to predict the coupling/decoupling phenomena occurring within the biotic bodies (e.g., antagonistic and synergistic effects of the elements) or the environment (e.g., Hedin et al. 1998; Li et al. 2000). Based on the concept of biogeochemical field, the dynamics of an ecosystem can be disaggregated into four components: primary drivers, biogeochemical field, biogeochemical reactions, and elemental cycles (Figure 3).

Quantifying the biogeochemical field for each specific ecosystem is an essential task for predicting biogeochemical processes and their environmental impacts. Any single change in the primary drivers such as climate, soil, herd size or type, feed or other management practices can simultaneously cause changes in several of the environmental factors (e.g., radiation, temperature, moisture, pH, Eh, and substrate concentration gradients); and any single change in the environmental factors can simultaneously affect several biochemical or geochemical reactions, which collectively determine the patterns and rates of elemental cycles in the ecosystem. For example, a change in house ventilation could simultaneously alter temperature, moisture, and substrate (e.g., $NH_3$) concentration gradients; these changes will simultaneously and collectively affect decomposition, $NH_3$ volatilization, nitrification and denitrification, which interact to determine how much N will ultimately be emitted from the house. It is almost impossible to determine a quantitative relationship between the cause (a change in ventilation) and the consequence (N gas emissions) through simple correlation or regression analysis. In addition, the extreme spatial and temporal heterogeneity of many of the primary drivers has

obscured the relationship between the causes and effects for many of the biogeochemical processes. That is why most of the correlations between a deviation in the primary drivers and the changes in biogeochemical cycles caused by the deviation are inherently non-linear, and even sometimes random or chaotic. The challenge is to describe this kind of complexity in a mathematical framework for prediction. The concepts of biogeochemistry were developed to provide the intellectual framework to help undertake this challenge.

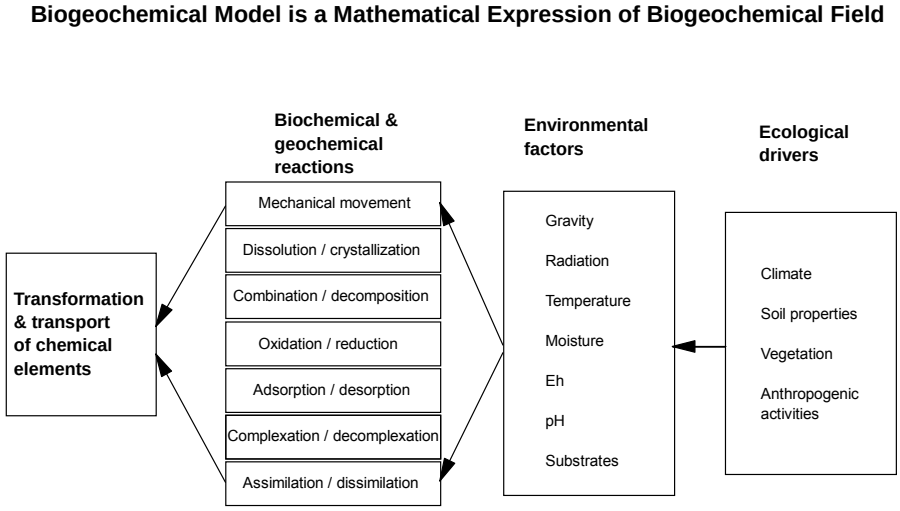


**Figure 3. The biogeochemical concepts utilized for modeling animal farm ecosystems**

Based on the above-described concepts, development of a biogeochemical model is to build bridges linking between the primary drivers (e.g., climate, soil, animal type and population, farm management practices) and the environmental factors (e.g., radiation, temperature, moisture, pH, Eh and substrate concentration gradients) as well between the environmental factors and the biogeochemical reactions. In Manure-DNDC, each of the seven farm components is described with two modules. The first module predicts dynamics of temperature, moisture, pH and Eh of the manure in the component; and the second module simulates decomposition, nitrification, denitrifiaction, fermentation and other biogeochemical processes for the manure in the component. The detailed parameters and functions defining the manure life cycle within a farm are summarized below and described in detail in Appendix A.

### *3.1.3. C and N Biogeochemistry of Manure Life Cycle*

Manure is produced in feeding lots where the animals are fed and rest. The manure stays in the feeding lot for a certain period and is then moved to storage or treatment facilities (e.g., compost, lagoon, digester). During the storage or treatment, the manure undergoes through a series chemical reactions that alter the manure's quality and quantity. The residue manure released from the storage or treatment facilities can be totally or partially applied in the field where forage crops could be planted. If the forage is utilized for feed in the farm, the manure

life cycle will be closed. Since Manure-DNDC was developed for predicting emissions of NH3 and greenhouse gases (i.e., $CO_2$, $CH_4$ and $N_2O$) from the manure life cycle, the biogeochemical processes have been installed in the model with a focus on C and N transport and transformation. By tracking the pools and fluxes of both C and N within the manure life cycle, insights about how the energy and nutrients of manure are transferred provide essential information to understand the environmental impacts of dairy farms. Figure 4 presents components of nitrogen cycling simulated in Manure-DNDC. The suite of C and N biogeochemical reactions which potentially occur in each of the farm components (illustrated in Figures 3 and 4) are described in Appendix A. Manure-DNDC model equations are listed in Table A-1.

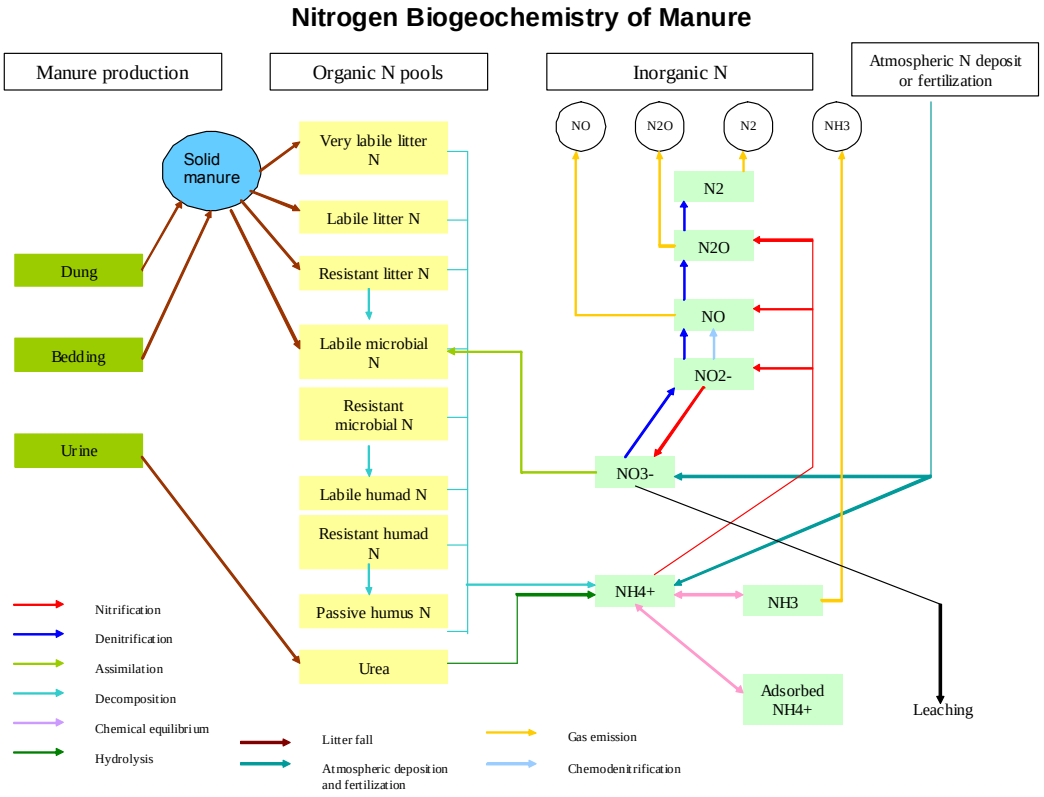


**Figure 4. Major nitrogen pools and fluxes of manure modeled in Manure-DNDC**

### *3.1.4. Enteric Gas Emissions*

This project mainly focused on development of Manure-DNDC framework and the processes affecting manure across the various farm components where the environmental parameters highly vary affected by weather, soil, farming management and facilities. Therefore, the gases produced from the physiological processes occurring in the digestive tract were not a central focus of our modeling efforts, so we adopted simple empirical equations to quantify the gas production rates from enteric fermentation. The equations were developed based on datasets

reported by researchers from their field or chamber experiments. Based on Mangino et al. (2007), daily enteric CH4 production is a function of the gross energy demanded by animal (Equation 20 in Table A-1 in Appendix A). Based on our experiments reported below, the enteric $N_2O$ and $CH_4$ fluxes from milk cow are about 0.001981 kg N/cow/day and 0.3859 kg C/cow/day, respectively (Equation 21 in Table A-1).

## 3.2. Greenhouse Gas Measurements

### *3.2.1. Environmental Chamber Study*

Experiments were conducted inside of an environmentally controlled chamber (4.4m×2.8m×10.5m) at the Department of Animal Science, University of California, Davis. The chamber (142 $m^3$ volume) has a continuous ventilation rate of 2,219 $m^3$/h (at 20°C and 1 atm), resulting in a chamber residence time of approximately 6 min and equivalent to 15.8 air exchanges per h. A balometer® (TSI Inc, Shoreview, MN) was used to check the ventilation rate before and after the experiment. The chamber temperature was maintained at 20°C and controlled via air conditioning. The relative humidity of air in the chamber was 56 ± 11 %. Typical dairy freestall housing conditions for three cows were simulated by assembling three steel freestall stanchions at the West end of the chamber where animals could rest. Head gates were installed at the East end of the chamber where cows accessed feed ad libitum. Animals had *ad libitum* access to water by a water trough. Ambient temperature and relative humidity were measured in 10 min intervals using two HOBO sensors (Onset Computer, Bourne, MA) located inside the chamber. Cow excreta (urine and feces slurry mix) accumulated on the concrete floor until the chamber was cleaned. The environmental chamber facility is certified by the Association for Assessment and Accreditation of Laboratory Animal Care International (AAALACI), and the Institutional Animal Care and Use Committee (IACUC) approved the project to certify the health and welfare of the animals.

#### *Animals*

The present work describes emission rates on a 'per cow' basis. The average body weights of dry and lactating cows were 770 and 656 kg, respectively and the feed intake (on a dry matter basis) was 17.7 and 19.1 kg per day, respectively. The average milk yield was 31 kg $cow^{-1}$ $day^{-1}$A total of nine dry (pregnant but not lactating) and nine mid-lactating Holstein dairy cows from the UC Davis dairy herd were used for the experiments in groups of three cows. Cows were fed a total mixed ration (TMR; Table 2) diet *ad libitum*, formulated to meet the 2001 National Research Council (NRC) requirements for either dry or lactating cows. Both diets were analyzed for crude protein (CP) (AOAC, 1997a), total digestible nutrients (TDN) (AOAC, 1997b), acid detergent fiber (ADF) (AOAC, 1997b), neutral detergent fiber (NDF) (Van Soest et al., 1991), and minerals (Ca, P, Mg, K; Sah and Miller, 1992). The chemical composition is listed in Table 2.

**Table 2. Diet ingredients used for dry and lactating cows.**

| | Dietary composition | |
|---|---|---|
| | **Dry cow** | **Lactating cow** |
| Grain | 0 | 34.8 |
| Alfalfa | 31.0 | 39.2 |
| Oat Hay | 61.0 | 0 |
| Whole Cottonseed Meal | 0 | 11.3 |
| Almond Hulls | 0 | 8.1 |
| Soybean Meal | 0 | 4.0 |
| Milk Mineral | 0 | 1.6 |
| Energy Mix | 0 | 0.6 |
| Salt | 0 | 0.3 |
| Dry Cow Pellet | 8.0 | 0 |

### *Gas Sampling and Analysis*

The environmental chamber has one incoming and one outgoing air duct. Analytical instruments located in the attic space above the chamber pulled air through Teflon tubing (12.7 mm ID, 0.25 m long) from each air duct immediately above the ceiling. Background samples of the 'empty chamber' were collected during the first day of each (two days) experimental period to assess the VOC and GHG concentrations in the incoming and outgoing air. After two h of empty chamber measurement, three cows were placed inside the chamber. The first two h after cows entered the chamber were used to measure air emissions in the 'cows only' phase (enteric fermentation; no manure). In the following 'cows and manure' phase, the animals were kept inside the chamber for additional 22 h and manure accumulated over time. The lactating cows were milked with a mobile milking unit before placement in the chamber and a second time inside the chamber at 19:00. After 24 h, cows were taken out of the chamber, but the accumulated animal manure was left undisturbed on the chamber floor for second day measurements (24 h; 'manure only' phase).

$N_2O$ and $CH_4$ from dairy cows and their excreta were continuously measured using an INNOVA model 1412 Field Gas Monitor (INNOVA AirTech Instrument, Ballerup, Denmark). This gas analyzer can selectively measure up to 5 component gases and water vapor simultaneously through the use of optical filters. The detection limits of the INNOVA 1412 are 0.21 $\mu g\ L^{-1}$ for $CH_4$ and 0.04 $\mu g\ L^{-1}$ for $N_2O$. In the present study, the INNOVA analyzer was calibrated monthly by the instrument manufacturer. The sampling interval for inlet and outlet air was 20 min. To avoid the responding error, only data logged between minute 5 and 17 of each sampling interval was used for later analysis. Data corresponding to the short interval of time when the chamber door was opened to allow entry and exit of cows (at 7:00 on the first day and 9:00 on the second day, respectively), were omitted for calculation of emission fluxes.

The emission flux rate was calculated using the equation:

$$E = \frac{\sum_{n} Q \times (C_{out} - C_{in})}{n \times N} \quad (1)$$

where:

$E$ = Gas emission rate from the chamber, mg cow$^{-1}$ h$^{-1}$,
$C_{out}$ = Mass concentration in the outlet air, mg m$^{-3}$,
$C_{in}$ = Mass concentration in the inlet air, mg m$^{-3}$,
$Q$ = Ventilation rate at 20°C and 1 atm, m$^3$ h$^{-1}$,

$n$ = Total effective measurement numbers,

$N$ = Cow numbers.

### *QA/QC Experiment*

QA/QC experiments were conducted to evaluate the performance of the environmental chamber and gas monitoring system. Pure $CH_4$ (Airgas Inc., Radnor, PA) was continuously and evenly distributed into the chamber through Teflon tubes at a flow rate of 1.3 L min$^{-1}$. The gas concentrations at the chamber inlet and outlet were continuously monitored using the INNOVA field gas analyzer that was used during the actual animal studies. Air ventilation rate was measured prior to and after the validation experiment. Background concentrations in the chamber were also measured for 24 hours prior to and after the validation experiment.

Mass balance calculation was conducted to evaluate the total recovery efficiency of the system. The recovery efficiency (*RE*) was calculated using the equation

$$RE = \frac{E'}{M_c} \times 100\%$$

$E'$ = Gas emission rate from the chamber during certain period, mg,

$M_c$ = Total gas mass input into the chamber during same period, mg.

### *Statistical Analysis*

The Proc Mixed procedure (SAS Inst. Inc, Cary, NC) was used for statistical analysis. The model comparing air emissions from dry and lactating cows included animal type (dry vs. lactating cows), time, and an animal type × time interaction with the groups (hosting different animals for each group) as the random factor. The model investigating the effects of animal and manure on air emissions included animal type (dry vs. lactating cows), phases (three periods of "animal only", "animal and manure", and "manure only"), and animal type by phase interaction. Groups were treated as a random factor. Time was a continuous variable; all others were categorical variables. For all measures, the predicted difference test in Proc Mixed procedure in SAS was used to separate means when the overall F-value was significant ($P<0.05$).

### 3.2.2. Cattle Pen Enclosure Study

A total of 96 pregnant, non-lactating Holstein cows were used to evaluate different waste management techniques in drylot corrals at the Environmental Quality Research Facility located at the University of California, Davis. Experiments were conducted during the periods of August 21 through September 25, 2006, and from April 13 through April 27, 2007. Animals were housed and treated in accordance with the Guide for the Care and Use of Agricultural Animals in Agriculture Research and Teaching (FASS, 1999), and the approved Animal Care and Use protocol for the University of California, Davis.

The cows were housed in the Cattle Pen Enclosure (CPE) facility, which consists of four, completely covered, dirt-floored corral pens (18.5 x 10 m each) that allow for simultaneous air emission testing of four mitigation treatments. Enclosures were oriented west (W) (front) to east (E) (back). A 10 m feed bunk, situated on a 3 m wide cement feed apron, was situated along the W side of each corral. The remainder of the corral was dirt floored with a 3% slope. In each corral, 14 locking head gates were situated along the feed bunk. A water trough with a float-activated water supply, providing the cows with *ad libitum* access to water, was located along the E side of the corral.

Each corral pen was enclosed with a CPE, a dome-like, 22 x 11 m structure (Figure 6). The construction was steel framed, consisting of welded truss arches with parallel 0.06 m diameter steel tubes spaced 0.3 m apart and strengthened by continuous 0.025 m diameter structural webbing that reached a height of 5.79 m at the top of the arch (36′ Legend Series Cover-all Building, Saskatoon, Saskatchewan, Canada). The steel construction was covered with a white Dura Weave cover, consisting of 100% Marquesa Lana with a double stacked weave (Intertape Polymer Group, Montreal, Quebec, Canada). The CPE was equipped with a roll-up door located on the E side, enabling cattle and equipment to be moved in and out of the facility. A feed flap, located on the W side of each CPE alongside the feed bunk, could be opened and closed as needed, and provides an efficient means of feed delivery into the bunks within each CPE.

Each CPE has a cooling pad on the E side to allow for air inflow and two fans in front of ventilation openings on the W side allowing for air outflow from the CPE. A panel, used to control cooling pad operation and fan speed, is located on the E side of each CPE. Two optical sensors (Monarch Instruments, Amherst, NH) are mounted on the two fans to provide constant monitoring of the fan's rotation rate per minute (RPM). The mA usage of each fan as well as the static pressure were recorded with data loggers (Onset Computer Corporation, Bourne, MA) at 10 minute intervals to allow for calculation of air flow. The 4.88 x 1.22 m cooling pad located on the E side of the CPE allows for ambient air inflow and also provides evaporative cooling as water runs down the pad using a pump (Beckett Corporation, Model W3500, Irving, TX).

Negative pressure is generated that is created by the fans blowing air out of the CPE. Due to the negative pressure mechanical ventilation (wind tunnel system) in each CPE, there is constant directional airflow from E to W within the CPE.

### *Experimental Treatments*

The study consisted of three replications of fourteen days each. The Holstein cows were randomly sorted into 4 groups of 8 animals each on day 1 of each period. Sorting occurred after the cows were weighed and the groups stratified by weight to ensure that the four randomized groups would be uniform in total weight. The four treatment groups were: 1) a control (CON); manure accumulation for 14 d without disturbance, 2) harrowing (HAR), which was raking three times weekly, 3) application of sodium bisulfate acidifier (SBS) on slurry, twice weekly, and 4) frequent corral scraping (SCR), once weekly. The four CPEs were randomly assigned a treatment, and this assignment was consistent throughout each replication of the study.

The CON did not experience any waste management technique intended to mitigate emissions. After the cows entered the CPE on day 1 of each experimental period, the waste was neither removed nor manipulated in any way for the entire 14 days. In addition, the cows assigned to CON remained in the enclosure for the entire period, with the infrequent exception of health checks and treatments of individual animals, usually lasting no longer than an hour.

On days 3, 5, 8, 10, and 12 of each experimental period, the corral surface of the CPE that was assigned to HAR was raked with a 4 x 4 chain harrow (Gearmore Inc., Model H4x4, Chino, CA). The cows were removed from the CPE and moved into an adjacent, open corral area while this treatment was implemented. The chain harrow was pulled on the back of a Honda all-terrain vehicle (ATV). This treatment took an average of 20 min. Upon completion of the harrowing treatment, the cows were moved back into the CPE.

On days 2, 4, 8, and 10 of each experimental period, SBS was applied to the ground surface of assigned CPE. The SBS acidifier was applied using a fertilizer spreader (Scotts®, AccuGreen 1000 Drop Spreader, Marysville, OH) at a rate of 0.37 kg/ $m^2$. SBS was spread evenly across the corral floor, on both the cement and dirt areas of the CPE. The animals were not moved out of the CPE during the time of application.

On days 5 and 12 of each 14 d period, the cows in SCR were moved from their CPE into an adjacent, uncovered dry lot corral for approximately one hour. During this time, the floor of the CPE was scraped, using a front loader (Bobcat, West Fargo, ND), and the manure was completely removed. The waste was moved away from the CPE and dumped into waste storage piles in a remote area to prevent possible contamination of inlet air. Once all manure was removed from the ground surface in the corral, the cows were moved back into the CPE.

### *Animal Performance*

In each period, the cows were weighed initially upon arrival to the facility (day 1) and again on the day of departure (day 14). Body weight (BW) was determined and average daily gain (ADG) calculated.

All animals were fed an identical total mixed ration (TMR) (Table 3) *ad libitum* once daily in the morning. The feed fed into each of the four CPE troughs was weighed at each feeding using the scale connected to the feed wagon (Kirby, Merced, CA). Feed amount was continuously

adjusted to allow for approximately 10% refusals. Feed refusals were collected daily and weighed prior to feeding.

**Table 3. Feed Ingredients in the Diet**

| Item | *% in diet*[a] |
|---|---|
| Feed Components | |
| Oat Hay | 42.80 |
| Cracked Corn | 22.13 |
| Alfalfa Hay | 17.31 |
| Almond Hulls | 13.43 |
| UC Davis Dry Cow Pellet[b] | 4.33 |
| Chemical Components | |
| Dry Matter | 93.1 |
| Protein | 10.75 |
| Ash | 6.39 |
| C | 45.4 |
| N | 1.77 |
| Ca | 0.54 |
| Mg | 0.24 |

[a] Reported on an a dry matter basis.

[b] UC Davis Dry Cow Pellet contained (%DM): 20.0 Crude Protein, 3.5 Crude Fat, 3.0 Crude Fiber, 2.8-3.3 Calcium, 1.0 Phosphorous, 0.8 Sodium, and 3.2 – 3.8 ppm Selenium.

Grab samples were taken from the refusals in each of the CPEs and from the feed wagon once weekly for dry matter analysis. The refusal samples were taken from five different areas within the trough and a composite sample generated. The samples were weighed and placed into an oven (Precision Scientific Co., Chicago, IL) at 107.2°C for 12 hrs. The five samples were weighed again, dry matter (DM) percentages of feed and refusals determined, and dry matter intake (DMI) of animals in each CPE calculated.

### *Animal Health*

Animal health was monitored by a veterinarian (SLB). Cows were observed upon arrival to the facility and throughout the duration of the trial. Individual animals that displayed any signs of poor health were examined more closely in a portable chute (Comfort Hoof Care, Model H*Series, Baraboo, WI), which was transported to the research facility as needed, and proper medical treatments were administered.

### *Environmental and Emissions Measurements*

Climatic measurements of ambient temperature (°C) and relative humidity (%) were measured continuously within each CPE. These climatic measurements were recorded using data loggers (HOBO Pro Data Logger Series, Onset Computer Corporation, Bourne, MA) that were placed above the feed flap inside each CPE. These temperature and relative humidity measurements were recorded at 10 min intervals. Climatic measurements were also taken from outside the CPEs using an automated weather system (Novalynx, Model 110-WS-16, Auburn, CA) at 15

min intervals. Measurements from the weather system included temperature, relative humidity, and black globe temperature (BGT).

### *Surface Measurements*

Measurements of soil pH and temperature were taken in all four CPEs once weekly. Additional pH and temperature measurements were conducted in the SBS treatment group 48 hours post treatment. Measurements were taken in ten different locations throughout the CPE using a portable pH meter (Fisher Scientific, Accumet AP84, Pittsburgh, PA) and a laser radiation thermometer gun (Raytek, Raynger ST, Santa Cruz, CA). The ten measurement locations were spread evenly throughout each CPE, in a grid fashion (Figure 7), and were representative of the entire enclosure.

### *Air Emission Measurements*

Greenhouse gases nitrous oxide ($N_2O$), methane ($CH_4$), and carbon dioxide ($CO_2$) were continuously measured using an INNOVA model 1412 Photoacoustic Field Gas-Monitor (INNOVA, AirTech Instruments, Ballerup, Denmark). This gas analyzer can selectively measure up to five component gases and water vapor simultaneously through the use of optical filters. The equipment was located in a centralized air conditioned cabinet outside of the second CPE. A total of 48.8 m of Teflon tubing (with 12.7 mm ID) was used to connect the equipment to all four enclosures. To minimize tubing length as a confounding factor, tubes in each enclosure were of identical length. Samples were sequentially taken at an inlet location and from the outlet locations in each of the four CPEs for twenty minutes at a time.

Gaseous concentrations and air flow were measured continuously and emission rates were calculated.

Emission rates (kg/cow/year) were calculated using the following equation:

Emissions = MIX*FL*60*1000*/22.4*MW*/1000000*24*365/cow#/1000

where:

MIX is the net concentration in ppm

FL is the ventilation flow rate ($m^3$/min)

60 is the conversion from min to hr

1000 is the conversion factor from $m^3$ to L

22.4 is the volume of one molar ideal gas at standard temperature (L/mole)

MW is molecular weight (g/mole)

1000000 is ppm

24*365 is the conversion from hours to year

cow# is the number of cows in each CPE (8)

and 1000 is the conversion from grams to kilograms.

#### *Statistical Analysis*

The statistical analysis of the $N_2O$, $CH_4$, and $CO_2$ emissions was completed using Proc Mixed procedures in SAS. Observations were repeated over time. The model included replication, treatment, day, and treatment*day interactions as fixed effects. The PDIFF option was added to an LSMEANS statement to test all possible pairwise comparisons between the four study treatments and was adjusted with Bonferroni and Tukey tests. Proc Mixed procedures in SAS were also used to statistically analyze the above gaseous emissions at day 0, prior to animals entering the CPEs, to insure that the enclosures did not differ prior to implementation of treatments. Animal performance measures (BW, ADG, and DMI) were analyzed using Proc GLM procedures in SAS. All data was analyzed at a significance level of $P < 0.05$.

### *3.2.3. Analysis of Rumensin on Enteric Fermentation*

Rumensin fed cows (RUM) were compared to untreated control cows (CON) with respect to the effects of the feed additive on greenhouse gas (GHG) emissions along with animal performance (dry matter intake ,DMI), milk production, milk components, plasma urea nitrogen (PUN), milk urea nitrogen (MUN), and the microbial population structure of fresh waste. Measurements of GHG were collected at days 14 and 60 in an environmental chamber simulating commercial dairy freestall housing conditions. Milk production and DMI measurements were collected twice daily over the 60 day experimental period and milk components, PUN, and MUN, were measured on days 14 and 60. The microbial population structure of 6 RUM and 6 CON cow fecal contents were examined on three different occasions.

## 3.3. FTIR Measurements of N2O Emissions

The project designed and developed an FTIR system to collect concentration data for nitrous oxide at 4 elevations, 1, 2, 5 and 10 meters and used a simple gradient model to give first order flux values. The data presented are the extractive measurements taken at two sites, specifically, one over a dry lot and one over a compost pile. The dry lot measurements consisted of almost continuous sampling for two months. These data provide a database for model validation. Specifically the long time sampling was performed to examine temporal fluctuations of emissions with the goal of understanding the impact of changing environmental conditions (e.g. rain events, temperature fluctuations) on $N_2O$ emissions from a dry lot. The compost pile measurements were collected to investigate potential differences in baseline emissions from compost piles and dry lots.

### *3.3.1. FTIR Suitability for $N_2O$ Measurements*

IR spectra for $N_2O$ was generated using certified calibration gas of 25 ppmV (which is approximately 75 times that found in ambient air) and measured in an 8-meter White cel1 that was heated at 20 C with pressure controlled at 740 torr.

The IR spectra for $N_2O$ can be found on Figure 5 and shows that there are two distinctly identifying regions for $N_2O$. The first occurs around the 2150-2250 $cm^{-1}$ region, with peak $N_2O$ absorbance occurring at approximately 2240 $cm^{-1}$. This region has been used as the defined characteristic absorption region for past FTIR $N_2O$ measurements. The second occurs around the 1250-1300 $cm^{-1}$, with peak $N_2O$ absorbance occurring at approximately 1290 $cm^{-1}$. Detection

limits were determined by using the generated calibration spectra at 25 ppmV and measuring the response of the FTIR to zero gas (contains no nitrous oxide) for the stronger responding 2150-2250 $cm^{-1}$ region. The minimum detection limit (MDL) at two times the standard deviation (2σ) of zero air response with five-second averaging was found to be 0.021 ppmV or 21 ppbV. Since background levels are approximately 315 ppbV, the FTIR with the 8-meter White Cell has a MDL that is 16 times more sensitive than background levels and is therefore highly suitable for these measurements.

Since the MDL is approximately 21 ppbV at five second integration, we expect that with thirty second integration, which we used, we will have sufficient resolution to detect changes of better than 10 ppbV from background as the technique has better sensitivity with longer integration times.

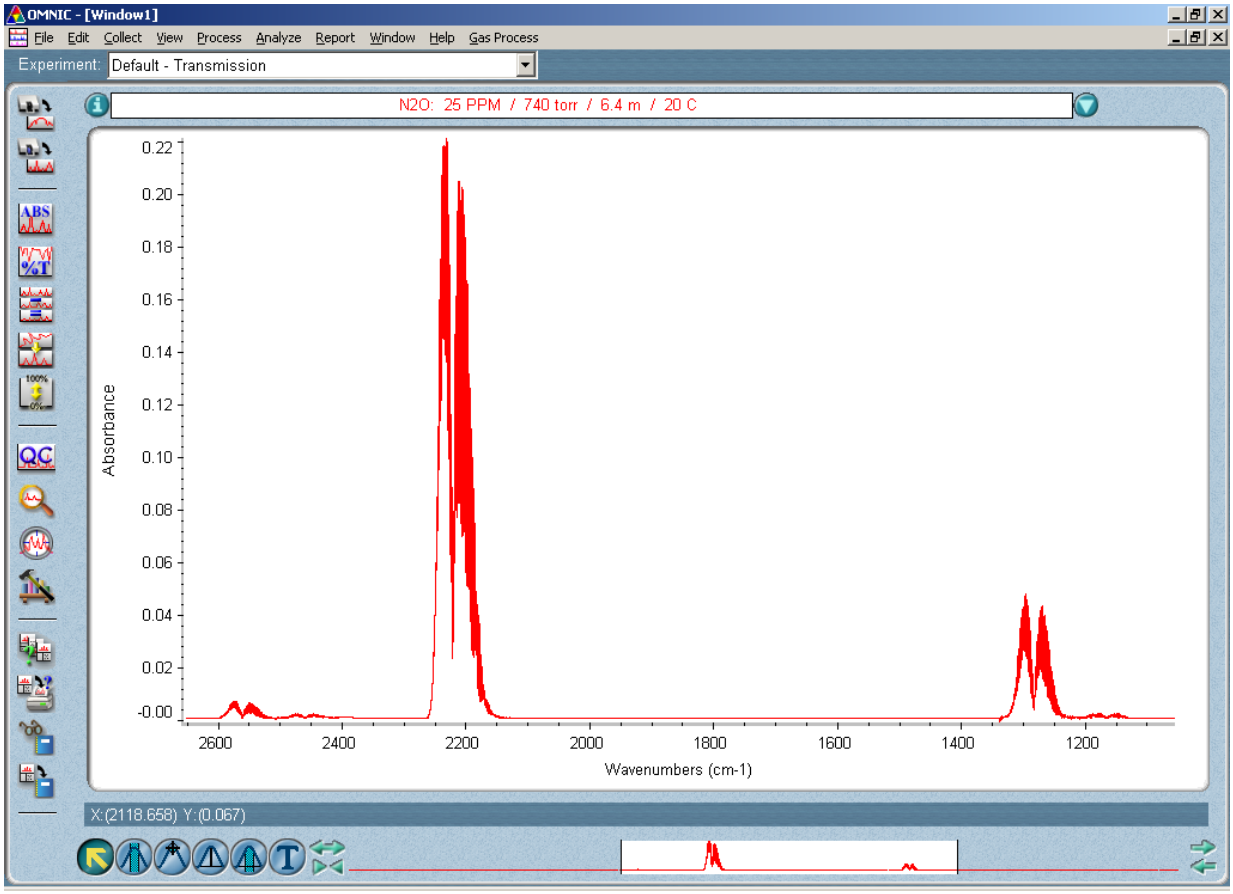


**Figure 5. Plot of $N_2O$ Spectra using 25 ppmV certified calibration gas into a 8.3-meter White Cell that was controlled at 10 C and 740 torr.**

### *3.3.2. Sampling Schedule*

A trailer, tower, meteorological sensors, and FTIR were set up on October 19, 2007 (see Appendix Bfor discussion of this setup). Trial sample runs of various durations were made

beginning at that time. On October 20, the system was set up to run essentially continuously 24 hours per day until December 12th, a period of nearly two months. As can be expected a large database was collected. CE-CERT provided oversight through October 26. During this time sampling was periodically interrupted to verify sample flow switching and to download data. From October 26 to December 12, 2007, the FTIR was operated by CSUF staff that filled the FTIR with liquid nitrogen twice a day. CE-CERT visited the site approximately weekly to verify operation and to download data. On February 8 and 9, 2008, the FTIR system was set up to measure N2O emissions from manure compost primarily to compare with baseline drylot emissions.

## 3.4. GIS Database Development

### *3.4.1. Cropland and Dairy Extent Database*

Contemporary cropland areas were defined principally using the California Department of Water Resources (DWR) land use survey database. The California DWR supports ongoing efforts to conduct county land use surveys on a frequent basis. Since 1950 the DWR has conducted over 250 land use surveys for all or part of California's counties. The main emphasis and detail of the surveys is agricultural land with the results of the surveys used to determine agricultural area for the survey year. Potentially, over 70 different crop types can be mapped in the survey.

The DWR land use database contains a spatial distribution of land use and cropland polygons for 42 of the 53 counties with irrigated cropland in California. The database includes descriptions of crop type, animal feeding operations (including dairies), and irrigation practices. The distribution of dairies for this study was derived from these county land use survey GIS databases for all major crop areas in California. The county data were obtained through the DWR website (http://www.landwateruse.water.ca.gov/basicdata/landuse/digitalsurveys.cfm). We created a spatial map showing locations of dairies by extracting all dairy polygons from the DWR tiles and stiching them together to create a basemap coverage of dairy locations. Our DWR dairy database contains 2300 polygons, covering an area of approximately 25,500 hectares. These dairy polygons do not include surrounding cropland areas that are owned and used by the dairies for crop production and land application of manure. The polygons represent the physical location of the dairies, including housing, dry lots, milking parlors, manure storage and treatment areas and feed production and feed bunk areas. The CDFA California Agricultural Resources Directory (2006) reported that there were 2,107 dairy operations in California. Figure 6 shows the density of dairies in California, expressed as the total area of dairies within 5 kilometer grid cells. It is clear that the majority of dairies are located on the central valley, with a few pockets of dairies in Riverside and San Bernardino Counties in southern California.

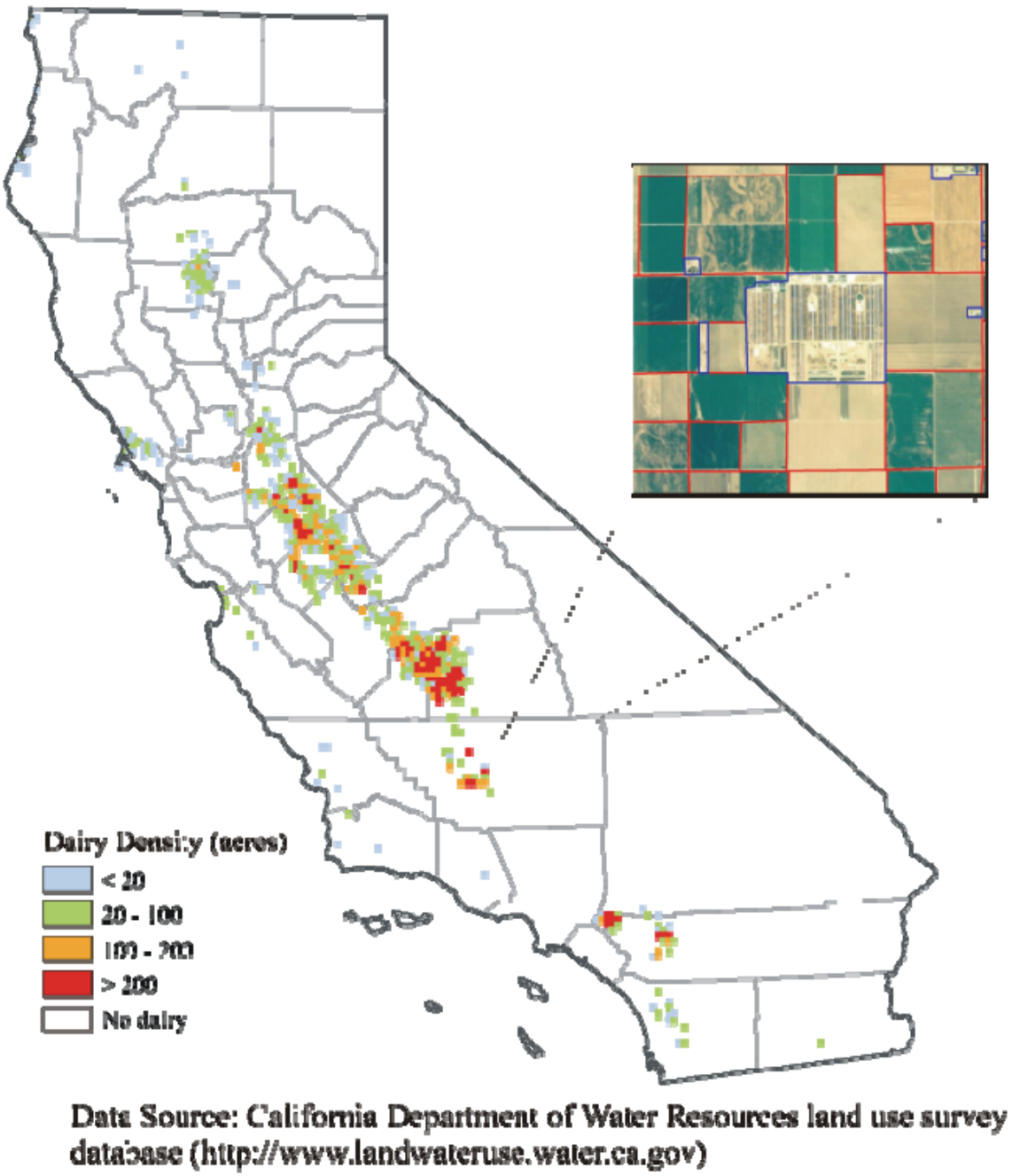


**Figure 6 Density of dairies in California. Outset shows the detail of the DWR land use databases overlay on aerial photo that was used to digitize the land use. A dairy is outlined in blue and surrounding crop fields are outlined in red.**

### *3.4.2. Climate Data*

The Manure-DNDC model requires daily climate data on precipitation, temperature, solar radiation and wind speed. We developed software scripts to automatically request and retrieve California Irrigation Management Information System (CIMIS) station data and reformat the

data to run with Manure-DNDC model. CIMIS provides data access to their database of over 120 stations throughout California via following two ways –

- Free ftp access. This dataset provides access to partial data covering only last few years. In addition single station data is subdivided to multiple files in multiple directories with inconsistent data formats. In addition some files are compressed and some not. Scripting of data retrieval tools from this free ftp site is straight forward, but some complicated due to complex data organization and very limited to available data range (dates).
- Membership access. While this one provides full access to CIMIS database, it requires registration and user/password login.

Since membership login provides access to full dataset we focused on this direction and developed the following set of tools that allow complete, automated data retrieval from CIMIS:

- "cimis_download_daily.pl" - Universal code for manual or automatic scheduled data downloads and daily updates of CIMIS DAILY data for one or given list of stations. The downloaded data is stored in a local file depository in DNDC daily data format.
- "cimis_download_hourly.pl" - Universal code for manual or automatic scheduled data downloads and daily updates of CIMIS HOURLY data for one or given list of stations. The downloaded data is stored in a local file depository in DNDC hourly data format.
- "cimis_coord_2_station.pl" - Supporting code to find a list of nearest CIMIS stations to given LON/LAT coordinates. The code give also distance and azimuth to those stations so that a user can choose which one is more appropriate for data retrieval and analysis.

The code has been tested to run on both Linux/Unix and MS Windows family of operating systems. We used these scripts to download climate data from all the CIMIS stations in the dairy production regions of California.

### *3.4.3. County Dairy Cow Statistics*

Annual statistics listing inventory of total cattle and milk cows were downloaded for all counties in California from the NASS website at http://www.nass.usda.gov/QuickStats. Inventories on head of total cattle, beef cows and milk cows were extracted for years 1975 through 2005. A cursory review of the database revealed missing data for several years for a number of the California Counties.

We identified 2004 as the target date for our modeling analysis. As an initial step in validating the database we identified counties with no milk cow entries for 2004. Thirty-one counties were identified as having a blank field for milk cow inventory in 2004. Historical milk cow inventory trends in the NASS database were then reviewed for the 31 counties to determine the extent and potential trajectory of dairy activity over the 30 year database time period. In addition, the California Department of Water Resources (DWR) irrigated areas GIS database was consulted to identify any dairy polygons in the 31 counties no milk cow inventory for 2004. Seventeen of the 31 counties had very low numbers of milk cows reported throughout the NASS census and most only reported through the early 1990's. Also, most of these counties did not have any

dairy polygons in the DWR GIS database. Based on historical information and trends it was assumed that these 17 counties had negligible or no dairies in 2004.

Fourteen of the 31 counties reported higher milk cow inventories through the end of the 1990's and in many cases also have dairy polygons in the DWR dataset. It was assumed that these counties represent areas where dairies were once active but have since been converted to other agricultural and/or land uses.

The two exceptions to this assumption were Imperial and Del Norte Counties. Both Imperial and Del Norte Counties have milk cow inventories listed for year 2005 but lack information for years 2001-2004. We assumed that dairy cows were present in 2004 but this information was not available to be entered in the NASS census. An estimate of milk cows for 2004 was derived for each county by scaling the 2005 milk cow inventory by total cattle (i.e., 2004 milk cows = 2005 milk cows/ 2005 total cattle * 2004 total cattle).

### *3.4.4. Dairy Soils*

Soil data on organic carbon content, pH, bulk density and soil texture, which are required for running the Manure-DNDC model, were compiled using the USDA's The Natural Resources Conservation Service (NRCS) - National Cartography and Geospatial Center (NCGC) Soil Survey Geographic (SSURGO) database. The SSURGO database represents the highest detail of geographic soil data developed by the NRCS-NCGC. The dataset was developed from digitizing soil survey maps revised as needed using aerial photos and other available information. The database is designed to be used for broad planning and management uses covering state, regional, and multi-state areas. The SSURGO attribute database based on the National Soil Information System national database gives the proportionate extent of the component soils and their properties for each map unit and includes over 25 physical and chemical soil properties, interpretations, and productivity. The SSURGO dataset was used to obtain the minimum and maximum ranges for the soil attributes required by DNDC (pH, clay content, bulk density, soil organic matter) for each of the Manure-DNDC spatial modeling units.

The SSURGO database is arranged in a multi-layer format, where each polygon (referred to as 'map unit' by SSURGO) can have multiple components and each component can have multiple layers. A soil component is a set of properties that is used to describe a certain soil type. The percent areas that each soil component occupies within the SSURGO polygons are provided ('*COMPPCT_R*' variable), however there is no information provided as to the actual spatial distribution of each component within the polygons.

It is evident that each SSURGO polygon has the potential for dozens of scenarios based on multiple soil components and layers; however the Manure-DNDC model requires a single set of input ranges for the soil input variables. In order to take advantage of the detail that is available in the SSURGO database, an area-weighted approach was used. First, all soil layers except the top layer were eliminated, since this layer is typically deeper than the rooting depth for most crops which is the depth used for Manure-DNDC simulations. Second, based on the *COMPPCT_R* variable, soil components greater than 10% (of the surface layer) were area-weighted to be used as Manure-DNDC soil inputs.

Several soil texture categories in the SSURGO dataset were identified that have 'no data' for the DNDC variables. These soil texture categories include: cemented, fragmented, ice, indurated, mucky-peat, muck, peat, unweathered bedrock, weathered bedrock, and variable. It was assumed that cropland would not occur on any of these soil texture types; thus data from these soil texture categories were excluded.

To generate our modeling database of soil input variables, area-weighted Manure-DNDC soil variables (clay fraction, bulk density, organic carbon, and pH) were calculated for each of the 2300 dairy polygons from the DWR dataset.

### *3.4.5. Dairy Manure Management Practices*

As part of our effort to build a process-based modeling system for estimating greenhouse gas emissions from California dairies, we collected data on manure management systems. A database of dairy manure management practices has been compiled from hard copy dairy permit applications provided by the San Joaquin Valley Air Pollution Control District (SJVAPCD) and the South Coast Air Quality Management District (SCAQMD). These permits contain general data on livestock inventory and management practices for 293 large dairies in the SJVAPCD (282 dairies) and SCAQMD (11 dairies) regions required to submit a permit application. A description of the data with general statistics on manure management practices in provided in a separate report (see Appendix C). It is important to note that these statistics represent the management practices found on larger (typically >800 head) California dairies in general because permit are not required for smaller dairies. According to CDFA California Agricultural Resources Directory (2006), in 2004 there were approximately 1,100 dairies in California with at least 500 head. So, our permit pool represents approximately a 27% sample of the dairies. The dairies represented by these permits contain just over 1,000,000 of the 1, 800,000 dairy cows in 2004 (CDFA).

Dairy cow permit data were assigned to the DWR dairy polygons using the inventory values provided in the manure management system dairy permit database based on the GIS addressing for each permit. Some manual assignment and reassignment of permits to individual DWR dairy polygons was required. Two permits near the towns of Bakersfield and Buttonwillow were not assigned to DWR polygons because there were no available dairy polygons within a 20 mile radius of these towns (i.e., all proximal polygons were already assigned to larger dairies). All remaining dairy polygons were assigned inventory based on a livestock density ratio derived from county level dairy statistics and dairy polygon area from the DWR database. Where needed the livestock density ratio was adjusted to account for existing inventory from the permit data. A comparison of livestock density by county for those counties containing polygons with assigned permit data yielded density values similar to county estimated values form the NASS dataset. By linking the permit database to the DWR GIS databases we are able to assign local soils and climate information to each of the individual permits. This enables us to model emission from each permit facility.

# 4.0 Discussion

## 4.1. Greenhouse Gas Emission Measurements

### *4.1.1. Environmental Chamber Measurements*

The validation results indicated that the environmental chamber is well suited to accurately measure GHG emissions from animals and waste. The mass balance calculation showed approximately 90% of the total $CH_4$ input into the chamber were recovered at the outlet. The background concentrations of $CH_4$ and $N_2O$ prior to and after the validation experiment were approximately 1.40 and 0.67μg $L^{-1}$, respectively

Upon entry of both dry and lactating cows into the chamber, $CH_4$ fluxes immediately increased indicating that enteric fermentation is the main process responsible for production of this gas ('empty chamber' vs. 'cows only' phases; $P<0.01$) (Fig. 7). After removal of cows from chambers ('manure only' phase), $CH_4$ flux went back to background levels ('empty chamber'; Table 4), indicating that fresh manure did not produce noticeable $CH_4$ fluxes ('empty chamber' vs. 'manure only; $P>0.05$). The emissions of $CH_4$ from dairy cows also showed a clear diurnal pattern; maintaining higher rates during the day than at night. Decreasing emission rate were found from 20:00 (when the light was turned off) to 8:00 the next day. Kinsman et al. (1995) reported a similar pattern, with fluxes increasing at 7:00 and decreasing at 21:00. Differences in $CH_4$ emissions between dry and lactating cows were anticipated and observed (Fig. 7, Table 4). Lactating cows produced approximately 1.3 times more $CH_4$ than non-lactating dry cows per animal ($P<0.01$). This difference can be largely explained by the larger amount of readily fermentable substrate (i.e. corn) in the lactating vs. dry cows' diet, necessary to meet the nutritional requirements for cows at this stage of milk production (Table 2) (Wilkerson et al., 1995). In the present study, the estimated emission rate of $CH_4$ averaged 12.35 g $cow^{-1}$ $h^{-1}$ from dry cows and manure, and 18.23 g $cow^{-1}$ $h^{-1}$ from lactating cows and manure, respectively. The average weights of dry and lactating cows were 770 and 656 kg, respectively. Therefore, per 500 kg livestock unit, the lactating cow produced approximately 1.7 times more $CH_4$ than dry cows, which is close to the ratio reported by Holter and Young (1992). The $CH_4$ fluxes observed in the present study for lactating cows were greater than the 13.03 g $cow^{-1}$ $h^{-1}$ determined for adult Holstein and Jersey cows (EPA, 1998;) that is being used by some air regulatory agencies. Since fresh manure did not produce noticeable $CH_4$ fluxes and under commercial conditions is usually flushed out of the animal housing area on average three times per day, the $CH_4$ emissions from animal housing components of a dairy can be estimated largely on animal emissions. Several recent reports showed 17.47 g $cow^{-1}$ $h^{-1}$of $CH_4$ flux from lactating cows' facilities (Kinsman et al., 1995; Sneath et al. 1997), which is in a good agreement with findings obtained in the present study.

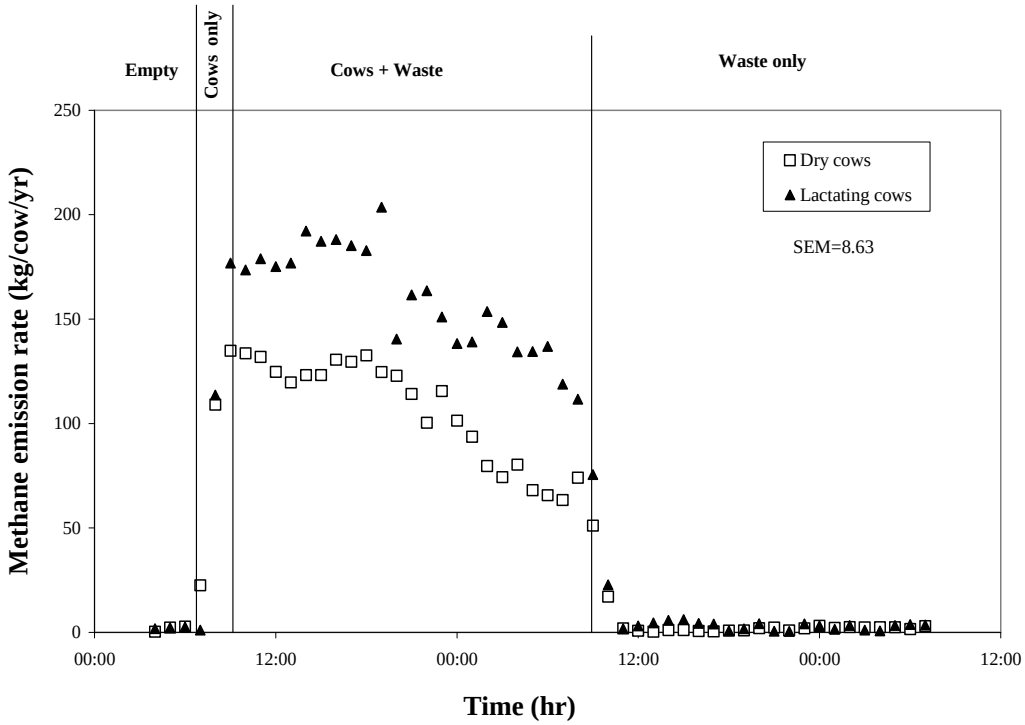


**Figure 7. Methane emission rates from three groups of dry and lactating cows (n=3), respectively. SEM = pooled standard error. Emission rates are expressed on a per year basis for easy comparison with annualizeg emission factors.**

**Table 4. Average methane emission rates from dairy cows and their fresh waste.**

| | Dry Cows | Lactating Cows |
|---|---|---|
| Average ethanol emission rate (kg $cow^{-1}$ $yr^{-1}$) | | |
| Empty chamber | 1.53 ± 0.28 | 1.31 ± 0.50 |
| Cows & Waste | 4.47 ± 0.74 | 11.13 ± 2.25 |
| Waste only | 2.93 ± 0.79 | 6.13 ± 1.40 |

[a] Standard error; (n = 3)

Kaspar and Tiedje (1981) reported that a small quantity of $N_2O$ can be emitted by the cow most likely produced during nitrate reduction reactions occurring in the gut. Nitrous oxide ($N_2O$) emissions showed clear increases (50-100 ppb) in outlet vs. inlet manifolds. Again, $N_2O$ emissions were released by the cows themselves rather than the fresh waste indicating that enteric fermentation in the animal's rumen might significantly contribute to this important GHG. Based on these finding, the present study estimates average direct $N_2O$ emissions from dairy cows of approximately 1 kg $N_2O$/cow/yr. Results from one group of lactating cows are shown in Figure 8. Although $N_2O$ emissions from cow enteric fermentation

appear to be minor on a per cow basis, additional research is needed to further study these emissions due to the large number of cows and the high GWP of nitrous oxide.

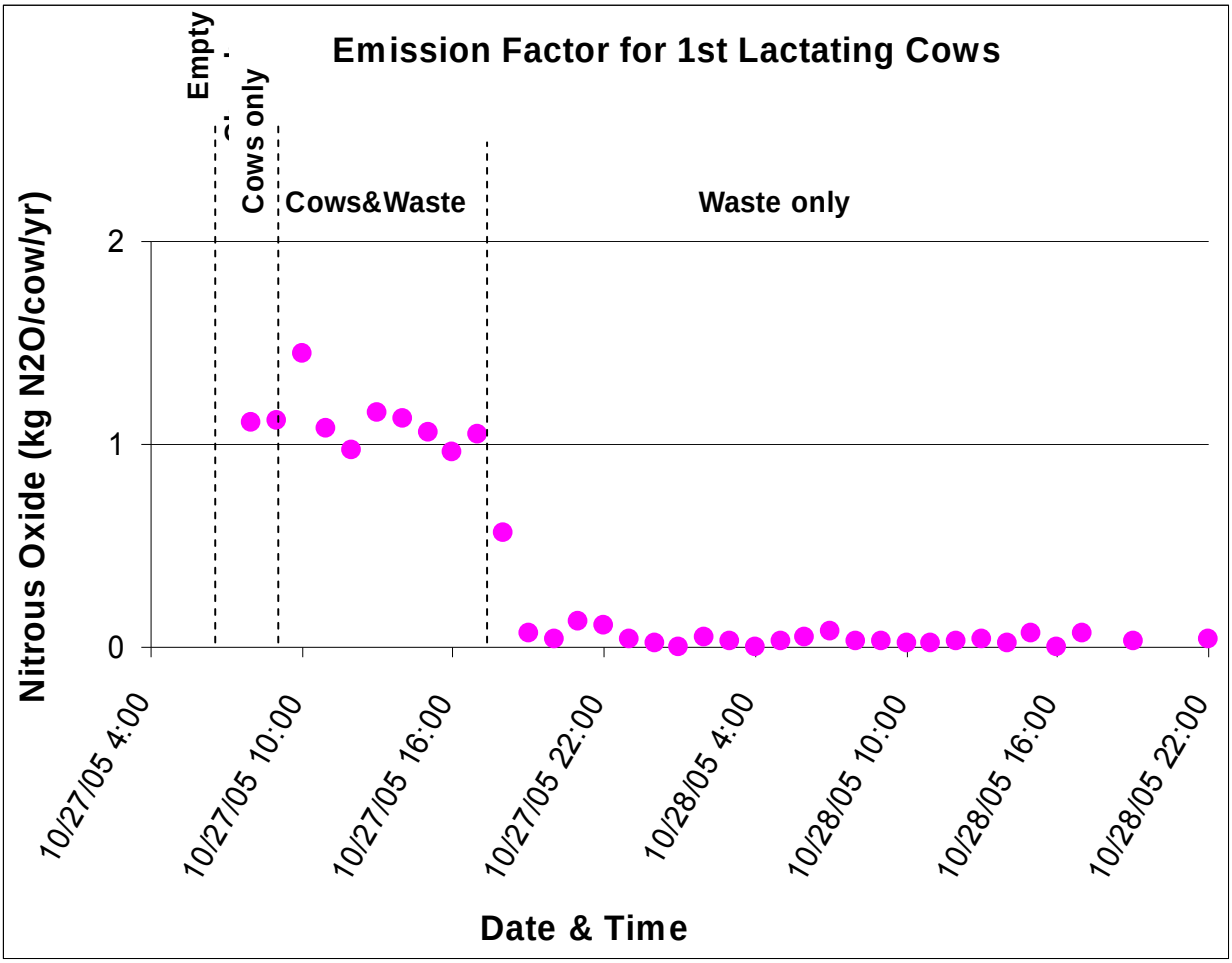


**Figure 8: Nitrous oxide emission from one group of lactating cows. Emission rates are annualized to facilitate comparison with annual emission factors commonly used in inventories.**

### *4.1.2. Cattle Pen Enclosure Study*

*Feeding and Body Weight Gain:* The mean initial BW of cows prior to entering the CPEs was 732.17 kg (ranging from 722.44 kg to 736.99 kg in the four treatment groups). The body weight did not differ across treatments (Table 5). On average, the cows gained 1.60 kg/head/day. Average daily gain ranged from 1.41 kg/head/day to 1.72 kg/head/day across the four treatment groups. Average DMI was 14.97 kg/head/day (ranging from 14.80 kg/head/day to 15.11 kg/head/day in the four treatment groups). Animal performance (ADG and DMI) were similar across the four treatments, but differed across the three replications (Table 5).

**Table 5. Least squares means, standard errors, and p-values for body weight at day 0, average daily gain, and dry matter intake [a].**

| | Treatment | | | | | P-values | |
|---|---|---|---|---|---|---|---|
| Item | SBS | HAR | SCR | CON | SEM | Trt | Rep |
| BW at day 0, kg | 733.21 | 736.05 | 736.99 | 722.44 | 8.19 | 0.91 | 0.004 |
| ADG, kg/hd·d | 1.62 | 1.72 | 1.41 | 1.64 | 0.33 | 0.74 | <.0001 |
| DMI, kg/hd·d | 15.09 | 14.80 | 15.11 | 14.87 | 0.27 | 0.90 | |
| | | | | | | | <.0001 |

[a] Every treatment was replicated three times and had eight non-lactating cows per replicate group.
SBS = Sodium bisulfate acidifier application treatment (two times / week)
HAR = Frequent harrowing treatment (three times / week)
SCR = Frequent scraping treatment (one time / week)
CON = Control

*Animal Health:* Two cows were observed limping during initial weighing in the chute prior to study treatments. Upon examination in a hydraulic hoof trimming chute (Comfort Hoof Care, Model H*Series, Baraboo, WI) they were observed to have toe ulcers (one from the first and one from the second replication) and were treated by opening and removing all damaged and necrotic tissue, bandaging, and placing orthopedic blocks on the opposite, sound claws. During the second replication, a cow in CON was found to have a white line abscess on the medial claw of the left rear hoof. This condition was treated by removing the undermined horn in the heel, opening the abscess, and placing a block on the lateral claw. A cow in SCR was found to have symmetrical swelling around the coronary band during the second study replication. No wounds were found, but swelling was more pronounced on the lateral side and there was evidence of trauma. The cow was treated with a non-steroidal anti-inflammatory drug (Banamine, Schering-Plough Animal Health, Kenilworth, NJ) and was given a parenteral antibiotic (Naxcel, Pfizer Animal Health, New York, NY) for three days. She recovered uneventfully.

One CON cow during day 12 of the first replicate aborted a 7-month old fetus. The fetus was taken to the California Animal Health and Food Safety Laboratory for diagnostic workup, which was inconclusive. The cow had a retained placenta and was lethargic and febrile. She was treated symptomatically with a non-steroidal anti-inflammatory drug (Banamine, Schering-Plough Animal Health, Kenilworth, NJ) and parenteral antibiotic (Polyflex®, Fort Dodge Animal Health, Fort Dodge, IA). She recovered and remained in the study. In the third replicate, a cow assigned to CON slipped on the concrete prior to being weighed on day 1. She was injured and was found to be non-ambulatory the following day. She was transported to the Veterinary Medical Teaching Hospital (VMTH), where she was treated by floating in a warm water bath (Aquacow rise system, St. Johnsbury, VT) several times and treated with fluids. She did not recover and was replaced in the study with another cow.

None of the health problems discussed above was thought to be a result of the study treatments.

*Climatic Measures:* Average outdoor ambient temperature ranged between 14°C - 23°C (Table 6) over the three periods. Average temperatures in the four CPEs during the experimental period were slightly lower than the outdoor temperatures, and ranged from 14°C - 20°C. Average outdoor ambient relative humidity ranged from 40% - 60% across the three experimental periods. Average relative humidity within the CPE was always higher than the outdoor relative humidity conditions, and ranged from 79% - 87%. Temperature and relative humidity within each of the four CPEs were similar and followed the same trends. Dramatic deviations (e.g., increase in temperature in a CPE) were only experienced temporarily and can be explained by factors that were immediately remedied, such as a broken pump in one of the enclosures.

**Table 6. Air temperature and relative humidity during the three experimental periods.**

| Climatic Parameter | Period 1<br>8/21/06 – 9/4/06 | Period 2<br>9/11/06 – 9/25/06 | Period 3<br>4/13/07 – 4/27/07 |
|---|---|---|---|
| Air temperature [a], °C | | | |
| Ambient | 22.59 ± 7.8 | 21.77 ± 6.6 | 14.53 ± 5.7 |
| Cattle Pen Enclosure [b] | 19.76 ± 6.0 | 18.04 ± 5.3 | 14.36 ± 5.8 |
| Relative Humidity [c], % | | | |
| Ambient | 52.73 ± 23.0 | 39.89 ± 19.4 | 60.31 ± 23.0 |
| Cattle Pen Enclosure [b] | 87.01 ± 19.6 | 82.88 ± 17.6 | 79.28 ± 25.4 |

[a] Average daily temperature ± standard deviation
[b] Average of measurements from all Cattle Pen Enclosures
[c] Average daily relative humidity

*Surface Measurements:* Average soil temperature measured once weekly (with each replication consisting of two weeks) was 19.58°C (ranging from 19.34°C – 19.76°C in the four CPEs). Average soil temperature was similar across the four treatments; however, there were differences within the CPE floor locations ($P = 0.02$) and over time ($P = < 0.0001$). Average soil pH, measured (figure 9 show the layout in the CPE and location of soil pH measurements) prior to first SBS application each week, differed across treatments ($P < 0.0001$). The average pH values ranged from 8.16 – 8.98 in the four CPEs, and the soil of the CPE assigned to SBS had a lower pH than the other three treatment groups. Average pH in CON, HAR, and SCR were similar across treatments.

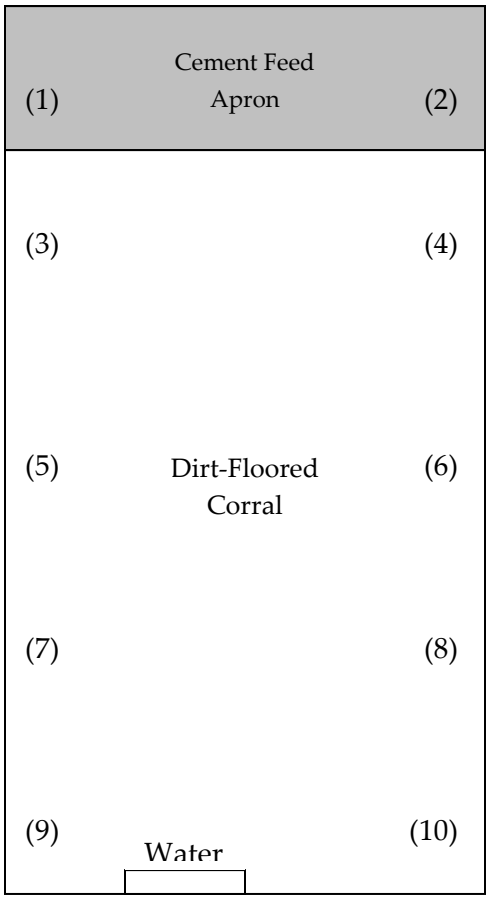


**Figure 9. Corral layout and sample location map for soil pH and temperature measures. The top of the corral, adjacent to the feed apron, faces west, and the back of the corral faces east. Numbers represent sampling locations.**

Soil measurements taken immediately prior to weekly SBS application compared with measurements made two days post application showed differences in temperature and pH ($P = < 0.0001$). Average temperatures were 19.58°C prior to SBS application and 17.53°C two days post treatment. Soil average temperatures in the SBS treated CPE varied over time ($P < 0.0001$). Average soil pH values were reduced by application of SBS acidifier, from a pre-treatment value of 8.16 to 4.53 two days post-treatment.

*Air Emissions:* Air emissions of $N_2O$, $CH_4$, and $CO_2$ did not differ across CPEs on day 0, prior to cows entering the enclosures and to the initiation of study treatments. Figures 10 to 12 show that day 0 gaseous emission factors were low and similar across treatments. Emissions increased drastically at day 1 when cows entered the CPEs and waste accumulation began. Gaseous emissions differed across replications (Table 7).

**Table 7. Gas emission rates provided as least squares means, standard errors, and p-values of nitrous oxide, methane, and carbon dioxide (in kg/cow/year)a for various treatments. SBS = Sodium bisulfate acidifier application treatment (two times / week), HAR = Frequent harrowing treatment (three times / week), SCR = Frequent scraping treatment (one time / week), and CON = Control**

| | Treatments | | | | | P-values | | | |
|---|---|---|---|---|---|---|---|---|---|
| Item | SBS | HAR | SCR | CON | SEM | Trt | Rep | Day | Day*Trt |
| $N_2O$ | 2.99 | 1.65 | 1.59 | 2.20 | 0.07 | <.0001 | <.0001 | 0.003 | 0.030 |
| $CH_4$ | 137 | 117 | 107 | 122 | 1.39 | 0.020 | 0.004 | <.0001 | 0.14 |
| $CO_2$ | 5929 | 6249 | 5659 | 6539 | 61.9 | 0.42 | <.0001 | <.0001 | 0.004 |

[a] Every treatment was replicated three times and had eight non-lactating cows per replicate group.

*Greenhouse Gases:* The emission rates for the greenhouse gases $N_2O$ and $CH_4$ differed across treatments ($P < 0.05$), but $CO_2$ emission rates were similar across treatments. All measured GHG emissions differed over time ($P < 0.05$).

Average $N_2O$ emission rates for SBS, HAR, SCR, and CON were 2.99, 1.65, 1.59, and 2.20 kg/cow/year, respectively. The $N_2O$ emissions were higher in SBS vs. the other treatments, and both HAR and SCR showed lower emissions than SBS and CON (Figure 10). Average $CH_4$ emission rates for SBS, HAR, SCR, and CON were 137, 117, 107, and 122 kg/cow/year, respectively. The SBS treatment group had the highest $CH_4$ emission rates (Figure 11), CON and HAR were similar, and SCR had the lowest emissions.

Average $CO_2$ emission rates for SBS, HAR, SCR, and CON were 5929, 6249, 5659, and 6539 kg/cow/year, respectively. $CO_2$ had a significant Day*Treatment interaction ($P = 0.0066$). Therefore, differences in $CO_2$ emissions between treatments are time dependant. Over time, all treatments differed in $CO_2$ emission rates. Lowest to highest emissions were in the SCR, SBS, HAR, and CON treatment groups (Figure 12).

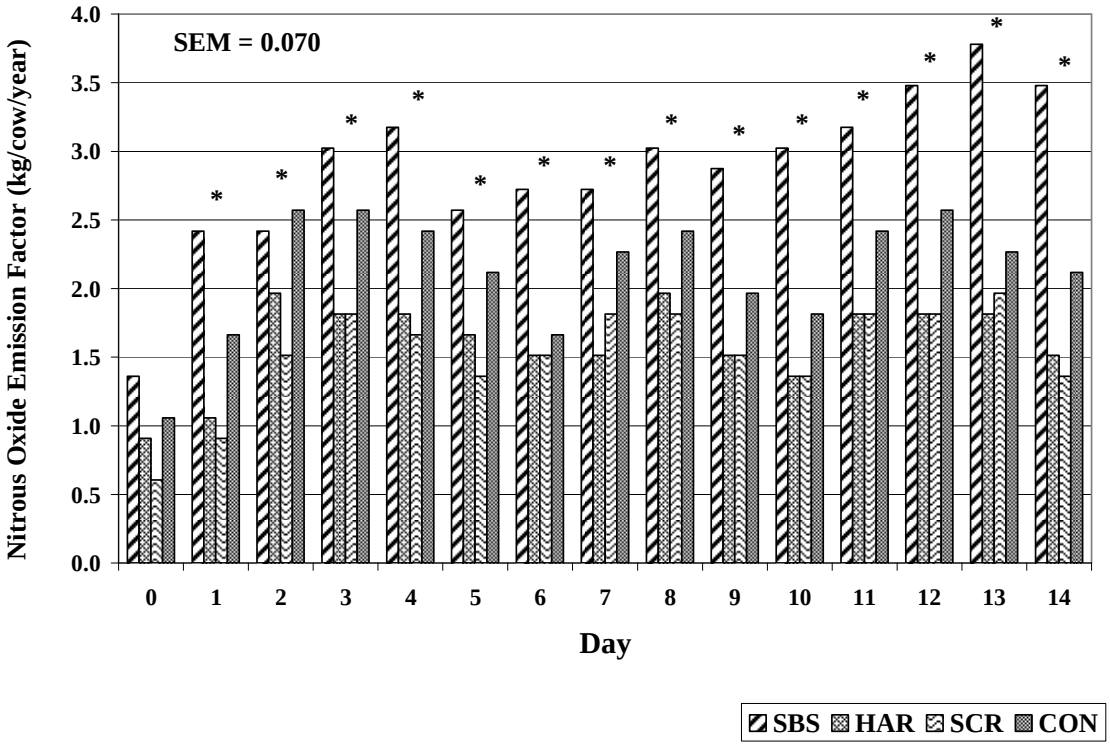


**Figure 10. Nitrous oxide emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.**

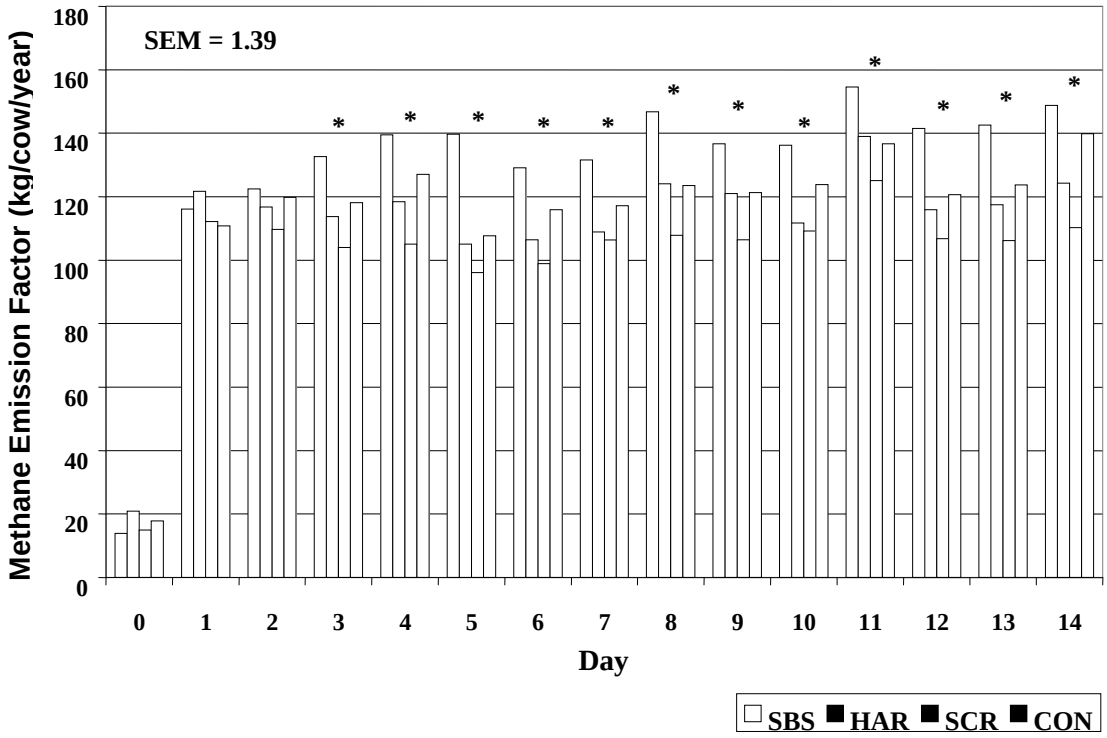


**Figure 11. Methane emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.**

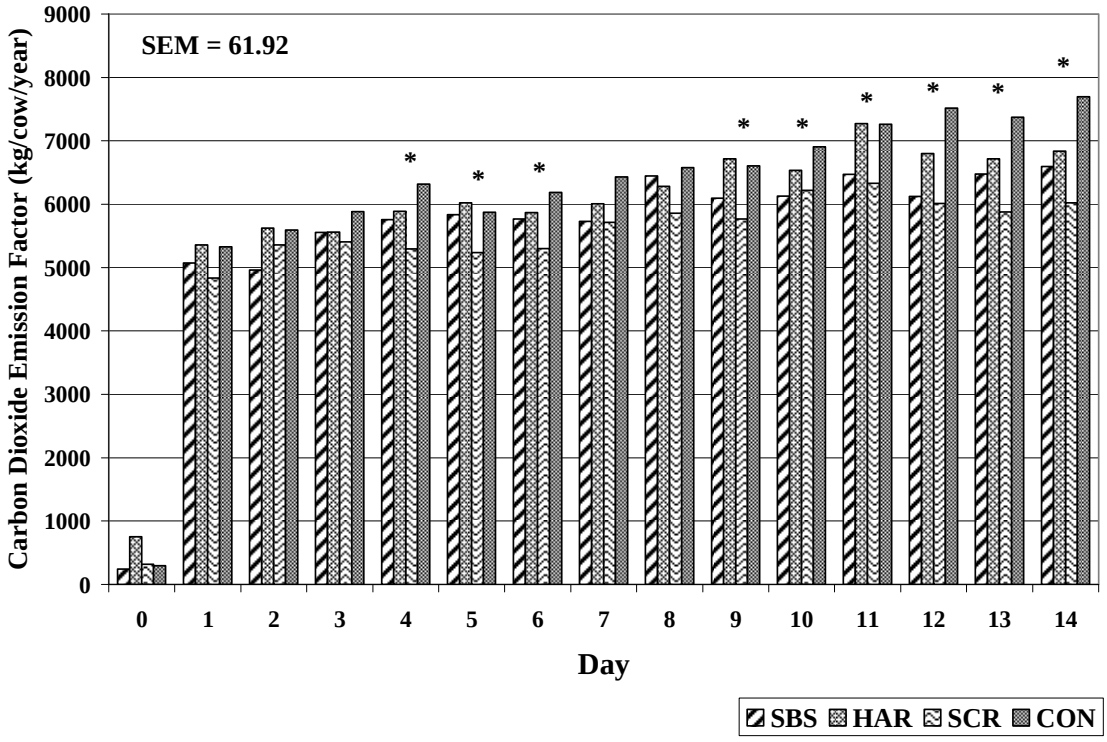


**Figure 12. Carbon dioxide emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.**

Application of SBS acidifier increased $N_2O$ and $CH_4$ emissions in the present study. Nitrous oxide emissions are primarily produced as a gaseous intermediate in the microbial process of denitrification. Denitrification is the stepwise anaerobic microbial reduction of nitrate ($NO_3^-$) to nitrogen gas ($N_2$) (Mosier et al., 1998a, Wrage et al., 2001). Several intermediates, including $N_2O$, are produced and could be emitted into the atmosphere (Wrage et al., 2001). Several studies have found that the proportion of $N_2O$ produced during denitrification increases at low pH (Nägele and Conrad, 1990, Daum and Schenk, 1998, Stevens and Laughlin, 1998). Therefore, it is not unexpected that the highest $N_2O$ emissions occurred in the more acidic conditions of the SBS treatment group. Higher $N_2O$ emissions are produced under acidic conditions because $N_2O$ reductase, the enzyme that catalyzes the reaction that converts $N_2O$ to $N_2$, is inhibited in low pH conditions (Knowles, 1982, Granli and Bøckman, 1994, Thomsen et al., 1994). The mechanisms resulting in the high emissions of $CH_4$ in the SBS treatment group are currently unknown and are not explained by the literature.

In the present study harrowing decreased emissions of $N_2O$, but did not affect the other measured gases. The process of harrowing aerates the soil and manure pack (Steinmann, 2002). Therefore, the microbes in the harrowed manure were introduced to oxygen. The measured

gaseous emissions result from processes from anaerobic bacteria. The results from the present study indicate that oxygen permeation of the manure due to harrowing is insufficient to inhibit methanogenic bacteria. However, the results suggest that the anaerobic process responsible for $N_2O$ emissions on dairies, denitrification, is hindered by the harrowing waste management technique. Research on the effect of harrowing on gaseous emissions is limited; however, a previous study by Steinmann (2002) showed that mineral nitrogen content was higher in harrowed soil when compared to a control. Therefore, harrowing may promote conditions that keep nitrogen in the soil rather than emitted into the atmosphere.

Completely removing waste from the corral areas by scraping once weekly reduced $N_2O$ and $CH_4$ emissions. Previous research by Osada et al. (1998) found that frequent removal of slurry from pig houses led to 10% reductions in $N_2O$ and $CH_4$ emissions.

Emissions of $CO_2$ did not differ across treatments. This outcome agrees with other work showing that the main source of the $CO_2$ from dairy cows is from enteric fermentation (Amon et al., 2001, Jungbluth et al., 2001). The experimental treatments implemented in the present study were waste management techniques and therefore were not expected to effect gaseous emissions emitted directly from cows in the processes of respiration and enteric fermentation.

### *4.1.3. Results of Rumensin Study*

Rumensin did not affect emissions of the GHGs methane ($CH_4$), nitrous oxide ($N_2O$), and carbon dioxide ($CO_2$. Over a 24-hour period, emissions of $CH_4$, $N_2O$, and $CO_2$ emissions decreased, while MeOH and EtOH emissions increased as waste accumulated on the chamber floor in both RUM and CON animals. Animal performance did not differ in RUM versus CON cows. Microbial population structure was similar between treatments.

### *4.1.4. FTIR Results*

#### *Dry Lot Measured Results*

Since the data was taken continuously for such a long period of time (almost two months) to combine the data set into a way that could be analyzed, a program was written using LabView to extract the data for each of the species, with respect to the height sampled. The data analysis software was written to extract the data per elevation at the $4^{th}$ point at each elevation as described earlier. The amount of data and the synch deviation from the FTIR to the valve control system required that the Labview program be written to extract the pertinent data point at each level and then search for the next synch point The data set was then assembled with corresponding meteorological data.

The goal was to estimate fluxes from the drylot to the north of the FTIR using the gradient flux method, thus the $N_2O$ data were screened for suitable periods with appropriate wind directions (from the North). Improvements to the $N_2O$ flux measurements can be made by using an open path FTIR measurement over the area source.

Appendix B contains plots of all the field data taken during the 2007 field measurement program. The data are presented in eight 7-day periods. This data set is extremely large and would require detailed analysis far beyond the scope of this project to try to estimate fluxes for

all the individual species and for all the times measured. Hence, here we report $N_2O$ flux measurements, representative periods of the data set, the concentrations of the other species only are presented here for completeness. These representative periods were selected using a program that matched the criteria of consistent wind speed and direction, clear discreet gradient to the surface as would be expected from a ground source.

Figure 13 depicts a typical representative spatial $N_2O$ distribution. Note that $N_2O$ levels near the surface are in the 365 to 385 ppbV range and that levels at 10 meters are around 340 ppbV, this is fairly consistent with most of the data set when winds were relatively constant in direction. Typically the levels of $N_2O$ measured were above nominal ambient measurements of 315 to 320 ppbV from the dry lot, showing a gradient to the 10 meter level. Detection limits were calculated in the lab to around 10 ppbV with the methodology developed for this project and the sampling time used. Note error levels were also usually in the plus or minus 10 ppbV range at two times the standard deviation of the signal noise over the sampling interval.

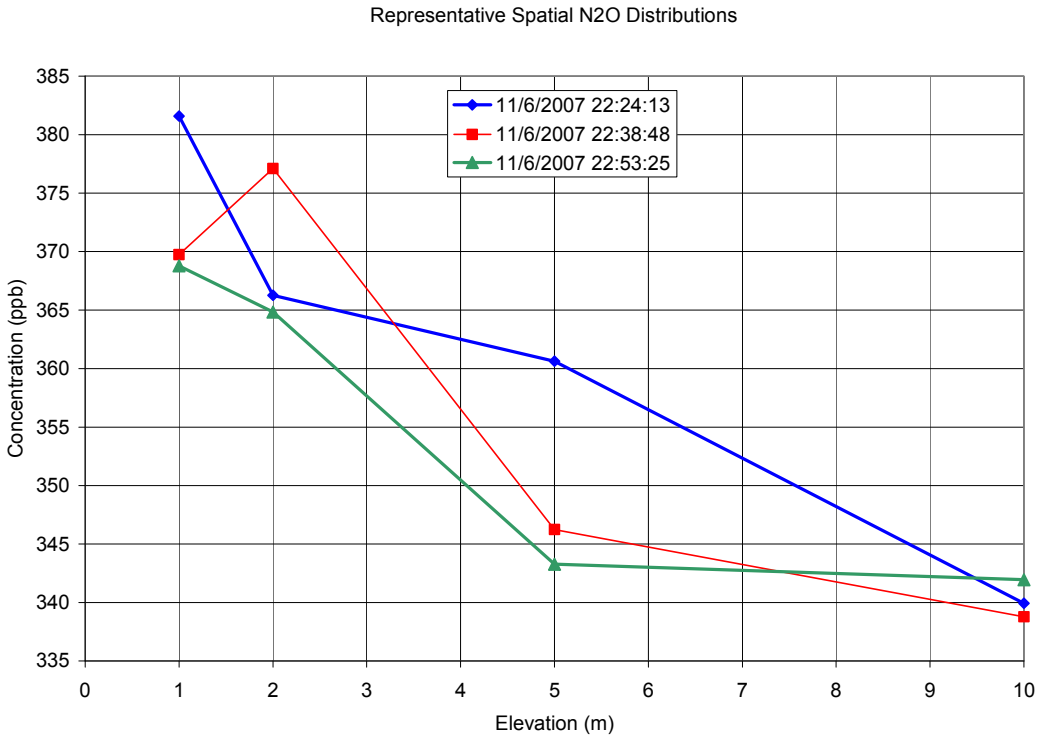


**Figure 13: Representative Spatial $N_2O$ Distributions to Each Measurement Height**

The goal of the long term measurements was to estimate baseline emission in the dry lot and to track changes in $N_2O$ emissions after a rain event. Such an event happened on December 7th. During the evening prior to the data reported here (Figure 14) 0.2 inches of rain precipitated. Note that $N_2O$ levels near the surface are in the 360 to 460 ppbV range and that levels at 10 meters are around 350-380 ppbV, this is fairly consistent with most of the data set when winds

were relatively constant in direction during a rain event. These levels are somewhat elevated when compared to normal dry lot conditions, by an average of 40-80 ppbV near the surface and 20 ppbV at 10 meters. However there were very few rain events during the period of sampling, so we are unable to assess if the observed changes in $N_2O$ concentration are consistent with changes in soil moisture or if the observed increases was due to other factors.

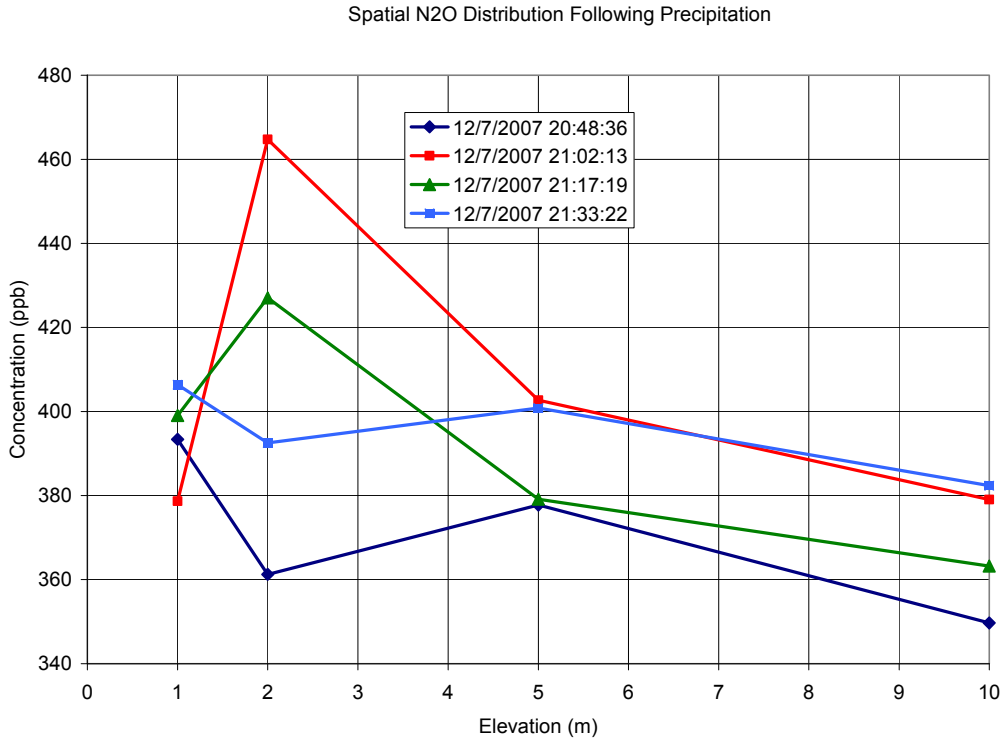


**Figure 14: Representative Spatial $N_2O$ Distributions to Each Measurement Height During a Precipitation Event (December 7th, 2007)**

Typical wind conditions were used to try and evaluate the $N_2O$ flux via the flux gradient method. Concentrations ranged from a high of 400 ppbV at the lower levels to a low of 365 at the highest elevation. This strong gradient observed under ideal conditions was used to estimate the flux of $N_2O$ via the gradient method for this period of sampling. However, do to variable wind conditions, likely contributions from surrounding area sources and noise, only a small subset of the data were deemed useful for estimating fluxes from the drylot area. The measured $N_2O$ fluxes over this study averaged from1.96 to 4.33 kg $N_2O$/ha/yr.

### *Compost Pile Results*

The FTIR system was setup with the sampling/meteorological tower over a compost site. Note that the winds were very weak and predominantly from the southwest blowing over the compost site. . Significantly, the compost pile was disturbed around 8:45 am, on the 9th of February. Average concentrations measured over the compost pile were slightly higher than

average concentrations measured over the feed lot, but what was really significant was that concentrations of $N_2O$ and $CH_4$ went significantly higher once the compost pile was disturbed. The observed average $N_2O$ concentrations were almost 5 times higher on average to those when the compost pile was left undisturbed. Figure 15 shows the data from just prior to the disturbance of the compost pile till just after. Further study into this and to the extent that compost piles are disturbed may lead to higher than expected $N_2O$ emissions from such practices. Also during this period there was a significant increase in $CH_4$ around 30% from disturbing the compost pile.

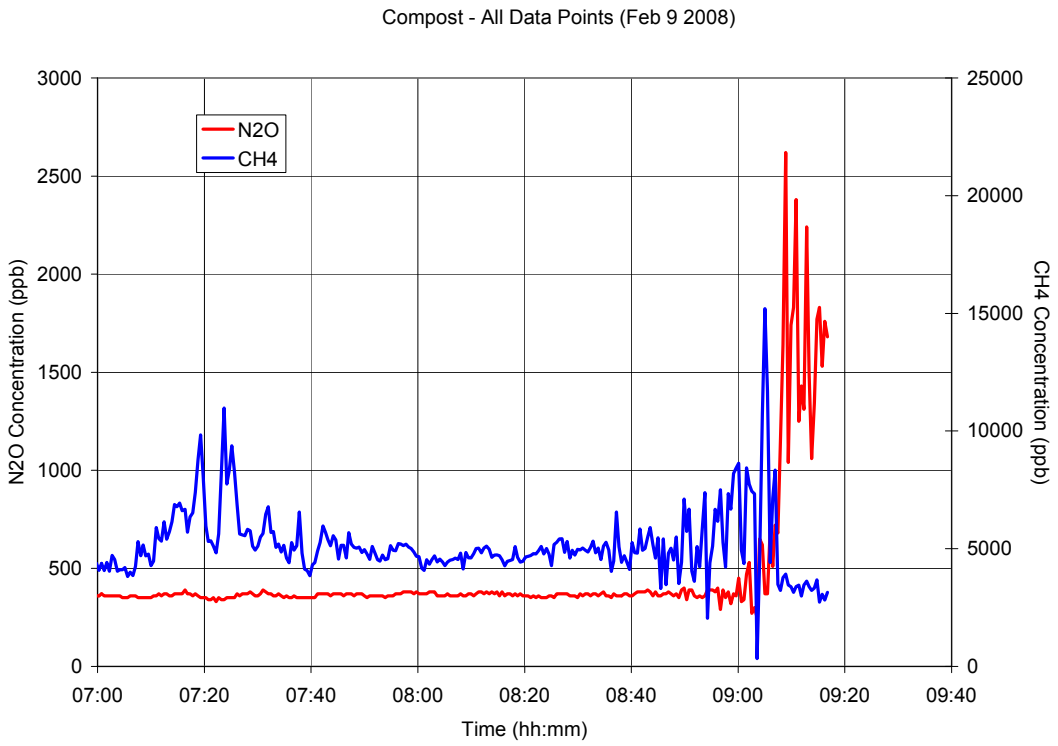


**Figure 15: Response of $N_2O$ and $CH_4$ Concentrations to Compost Disruption. The pile was disturbed just before 9am (exact time is not known).**

## 4.2. Manure-DNDC Model Validation

Manure-DNDC was tested against four datasets observed for animal farms in California and North Carolina. These validation cases were performed by providing the model inputs and then comparing model outputs with measured data. The three California dataset were analyzed to validate components of Manure-DNDC. The project analyzed a data set for a swine facility in North Carolina to test the ability of the modeling system to track the mass balance of nitrogen as it flowed through various stages of manure management.

***Case 1: $CO_2$, $CH_4$ and $N_2O$ emissions from cattle pen enclosure study***

The project measured $CO_2$, $CH_4$ and $N_2O$ emissions from a cattle pen enclosure for 14 days in 2007. During the experimental period, manure was continuously accumulated on the floor of

the cell. Temperature: 19.5 °C; feed rate: 15 kg DM/head/day and 10.75% as protein. Manure pH 8.8. The concentrations of the three gases were measured with the influx and efflux air samples at hourly time step. The gas fluxes were calculated based on the air flow rates with the gas concentrations, and converted to daily fluxes. The observed data indicated the emission rates of all the three gases slightly increased during the 14 days (Figure 16).

Manure-DNDC was run with a scenario: 8 beef cows; feed rate 15 kg DM/head/day with crude protein concentration 10.75%; cell floor area 100 m2 with concrete surface; no bedding; air flow rate 1320 cubic feet/min. The animal respiration rate and enteric $CH_4$ and $N_2O$ fluxes were simulated based on the routines of enteric gas production embedded in Manure-DNDC; and the manure-induced $CO_2$, $CH_4$ and $N_2O$ fluxes were quantified based on biogeochemical processes in the model. The total emission rate is the sum of the enteric sources and the manure-induced fluxes. The modeled daily $CO_2$, $CH_4$ and $N_2O$ fluxes are basically in agreement with observations. The modeled results indicate that (1) the enteric source dominated the gas fluxes and (2) the observed increasing trends in the gas fluxes during the experimental period were mainly driven by the gases emitted from the manure accumulated on the floor while the modeled respired $CO_2$ or enteric $CH_4$ and $N_2O$ emission rates were constant (Figure 16 and Table 8).

***Case 2: N2O, NH3 and CO2 emissions from drylot manure pack in CSUF***

A 6-day experiment was conducted by Dr. Charles Krauter and his colleagues to test the impacts of rainfall event on $N_2O$, $NH_3$ and $CO_2$ emissions from aerobic compost in CSUF in November 2006. Simulated rainfall was applied to the manure pack. Fluxes of $N_2O$, $NH_3$ and $CO_2$ were measured before and after the artificial rainfall event. The field data indicated that the rainfall stimulated $N_2O$ and $CO_2$ emissions while depressed $NH_3$ fluxes (Figure 17).

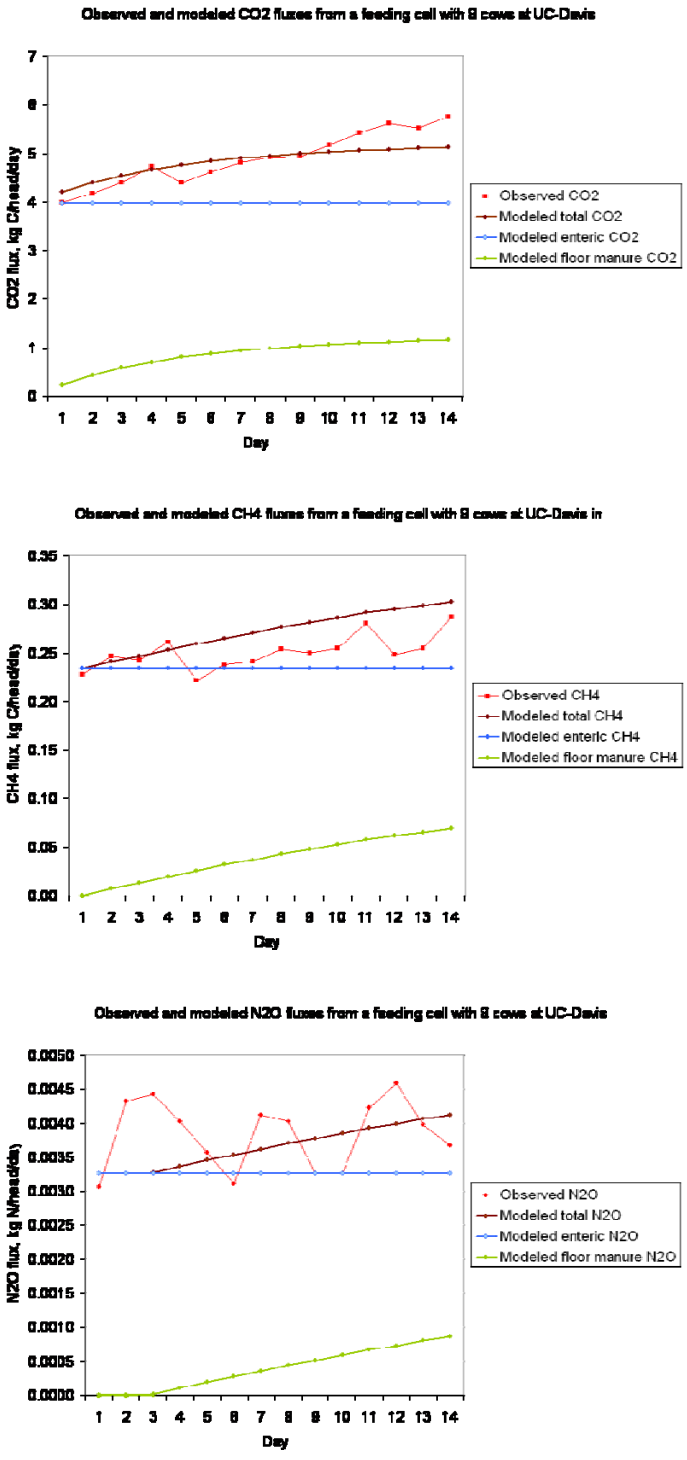


**Figure 16. Comparison between observed and modeled daily $CO_2$, $CH_4$ and $N_2O$ fluxes from a closed feeding cell with eight cows in UC-Davis in 2007. The modeled results indicate that the observed trends in the gas fluxes during the experimental period (14 days) were mainly driven by the gases emitted from the manure accumulated on the floor while the modeled respired $CO_2$ or enteric $CH_4$ and $N_2O$ emission rates were constant.**

**Table 8. Measured and modeled $N_2O$, $CO_2$ and $CH_4$ fluxes from CPE at UC-Davis in 2007**

| Day | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Observed N2O* | 0.0031 | 0.0043 | 0.0044 | 0.0040 | 0.0036 | 0.0031 | 0.0041 | 0.0040 | 0.0033 | 0.0033 | 0.0042 | 0.0046 | 0.0040 | 0.0037 |
| Observed CO2** | 3.98 | 4.18 | 4.40 | 4.72 | 4.39 | 4.62 | 4.80 | 4.92 | 4.94 | 5.16 | 5.43 | 5.62 | 5.51 | 5.75 |
| Observed CH4** | 0.23 | 0.25 | 0.24 | 0.26 | 0.22 | 0.24 | 0.24 | 0.25 | 0.25 | 0.25 | 0.28 | 0.25 | 0.25 | 0.29 |
| Modeled total N2O | 0.0033 | 0.0033 | 0.0033 | 0.0034 | 0.0035 | 0.0035 | 0.0036 | 0.0037 | 0.0038 | 0.0039 | 0.0039 | 0.0040 | 0.0041 | 0.0041 |
| Modeled total CO2 | 4.20 | 4.39 | 4.54 | 4.67 | 4.76 | 4.84 | 4.90 | 4.95 | 4.99 | 5.03 | 5.05 | 5.08 | 5.10 | 5.11 |
| Modeled total CH4 | 0.23 | 0.24 | 0.25 | 0.25 | 0.26 | 0.27 | 0.27 | 0.28 | 0.28 | 0.29 | 0.29 | 0.30 | 0.30 | 0.30 |
| Modeled enteric N2O | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 | 0.0033 |
| Modeled floor manure N2O | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0002 | 0.0003 | 0.0004 | 0.0004 | 0.0005 | 0.0006 | 0.0007 | 0.0007 | 0.0008 | 0.0009 |
| Modeled enteric CO2 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 | 3.9625 |
| Modeled floor manure CO2 | 0.2363 | 0.4300 | 0.5788 | 0.7025 | 0.7988 | 0.8763 | 0.9375 | 0.9875 | 1.0288 | 1.0625 | 1.0900 | 1.1138 | 1.1338 | 1.1513 |
| Modeled enteric CH4 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 | 0.2338 |
| Modeled floor manure CH4 | 0.0000 | 0.0075 | 0.0125 | 0.0188 | 0.0250 | 0.0313 | 0.0363 | 0.0425 | 0.0475 | 0.0525 | 0.0575 | 0.0613 | 0.0650 | 0.0688 |

* Unit: kg N/day

** Unit: kg C/day

Manure-DNDC simulated the experiment with manure pack containing 5,200 kg DM with density 200 kg DM/m3. The modeled results indicated that watering the manure pack elevated the manure moisture and hence increased rates of decomposition, nitrification and denitrification that led to increases in $CO_2$ and $N_2O$ emissions. The addition of water diluted $NH_3$ concentration and reduced $NH_3$ volatilization rate. However, the modeled high $CO_2$ emissions lasted longer than observations (Figure 17). Validation results are also provided in Table 9.

**Table 9. Measured and modeled $NH_3$, $N_2O$ and $CO_2$ fluxes from manure pack before (Day 0) and after (Days 1-5) receiving a simulated rainfall at CSUF in 2006**

| Day | Field $NH_3$ | field $N_2O$ | Field $CO_2$ | Model $NH_3$ | Model $N_2O$ | Model $CO_2$ |
|---|---|---|---|---|---|---|
| 0 | 9.33 | 0.05 | 279.73 | 9.00 | 0.040 | 106 |
| 1 | 1.65 | 0.63 | 1034.31 | 2.00 | 0.860 | 1136 |
| 2 | 3.36 | 0.10 | 1119.89 | 2.00 | 0.720 | 1140 |
| 3 | | | | 3.00 | 0.020 | 1127 |
| 4 | 0.77 | 0.02 | 376.42 | 4.00 | 0.020 | 1105 |
| 5 | | | | 5.00 | 0.020 | 1073 |

* Units: kg N or C/day

***Case 3: N2O emissions from dry lots in CSUF***

Micrometerological method (FTIR) was applied for drylot measurements at CSUF dairy. The farm had 8000 m2 for the dry lots with 34 cows and 78 heifers. The manure was scripted four times per year. The measurement was conducted from 10/26/07-12/13/07. The measured results were treated based on the wind directions. The results showed that the daily $N_2O$ fluxes varied between 0.3 and 0.6 kg N/day for the farm.

Manure-DNDC simulated the case by setting a virtual farm with a outdoor pen having 34 dairy cows and 78 veal cows. Both the groups were fed with feed 15 kg DM/head/day containing 15% crude protein. The ground surface area of the pen was 8000 $m^2$. The manure on the ground was totally removed every 90 days. The modeled results indicated that moisture of the manure on the ground was low most time during the year, and hence neither nitrification nor denitrification became active. The enteric source dominated $N_2O$ emitted from the farm. The modeled $N_2O$ emission rates were around 0.5 kg N/day that is in the range of observations (Figure 18).

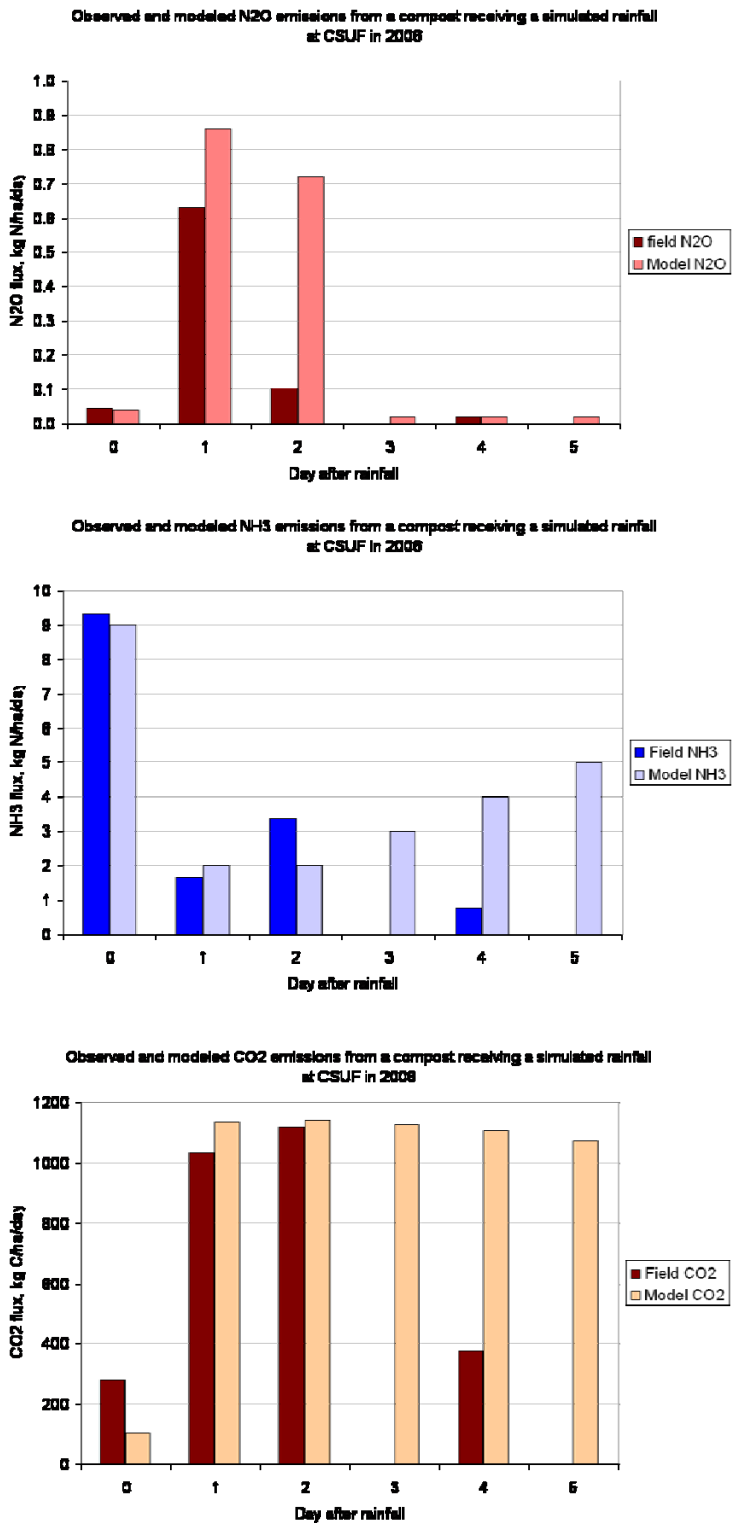


**Figure 17. Comparison between observed and modeled impacts of rainfall on $N_2O$, $NH_3$ and $CO_2$ fluxes from an aerobic compost in CSUF in 2006 (field data from Charles Krauter).**

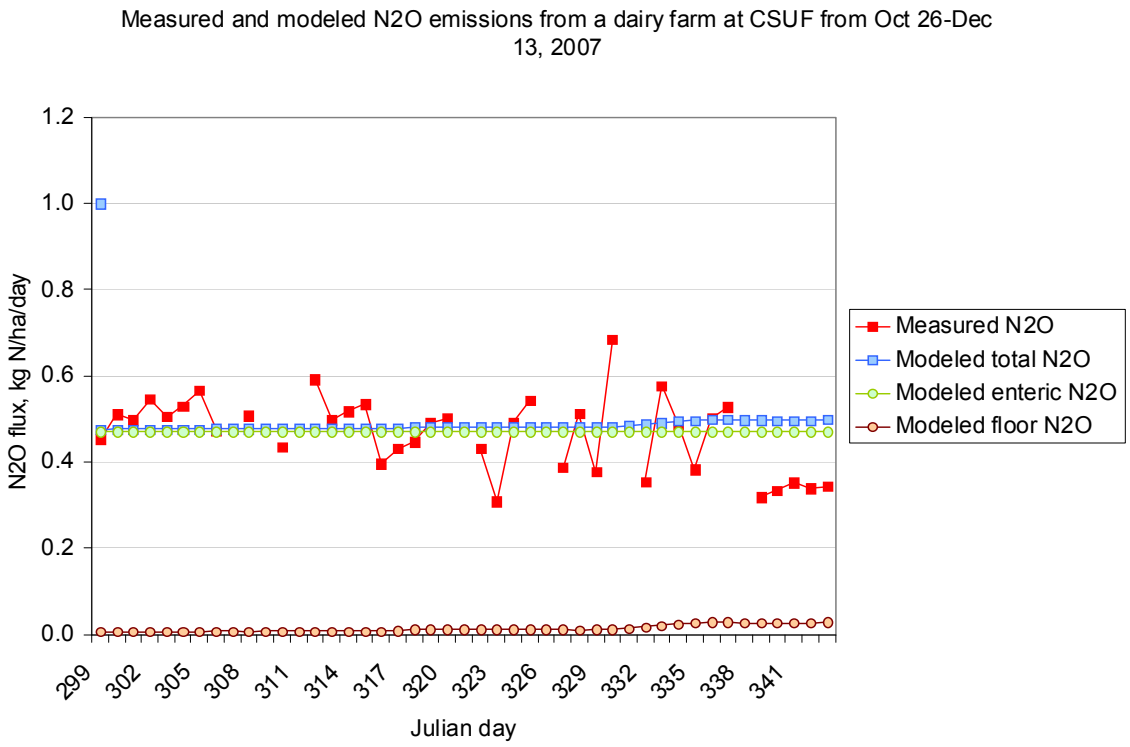


**Figure 18. Measured and modeled $N_2O$ emissions from a dairy farm with dry lots in CSUF in 2007**

*Case 4: N fluxes in a swine farm in North Carolina*

Harper and his colleagues conducted a 2-year experiment at a swine farm in the Coastal Plains of North Carolina in 1997-1998. This farm had 1200 sow (farrow-to-finish). The waste produced in house was directly transported to the lagoon. The dimension of lagoon was 256x85x3.1 m. The life time of the slurry in the lagoon was 15 years. They measured (1) the N contents in feed, milk, meat, feces, urine, lagoon slurry and field crop and soil, and (2) emissions of $NH_3$, $N_2O$ and $N_2$ from housing, lagoon and field where the lagoon slurry was applied as fertilizer. Based on the two-year measurements, they closed the N budget within the farm scale. The field data indicated that (1) housing and lagoon shared similar magnitude of $NH_3$ emissions and (2) denitrification-induced $N_2$ dominated N efflux from the lagoon.

Manure-DNDC simulated the case by constructing a swine farm with 1200 swine on a slatted floor with under-floor gutter. No bedding. Feed rate was 8 kg DM/head/day containing 0.35% crude protein. Manure was transferred from the house to the lagoon at daily time step. The lagoon had capacity of 67,456 $m^3$, surface area 21,760 $m^2$, no cover, receiving rain water, 20% of the slurry was transported to the field every 100 days. The 50 ha of field was planted with corn. The field soil was loam with pH 7.0, SOC 0.01 kg C/kg, and bulk density 1.4. One year simulation was conducted. The simulated results were basic in agreement with observations

(Figure 19 and Table 10). Lagoon played an important role in getting rid of excess N from the manure life cycle.

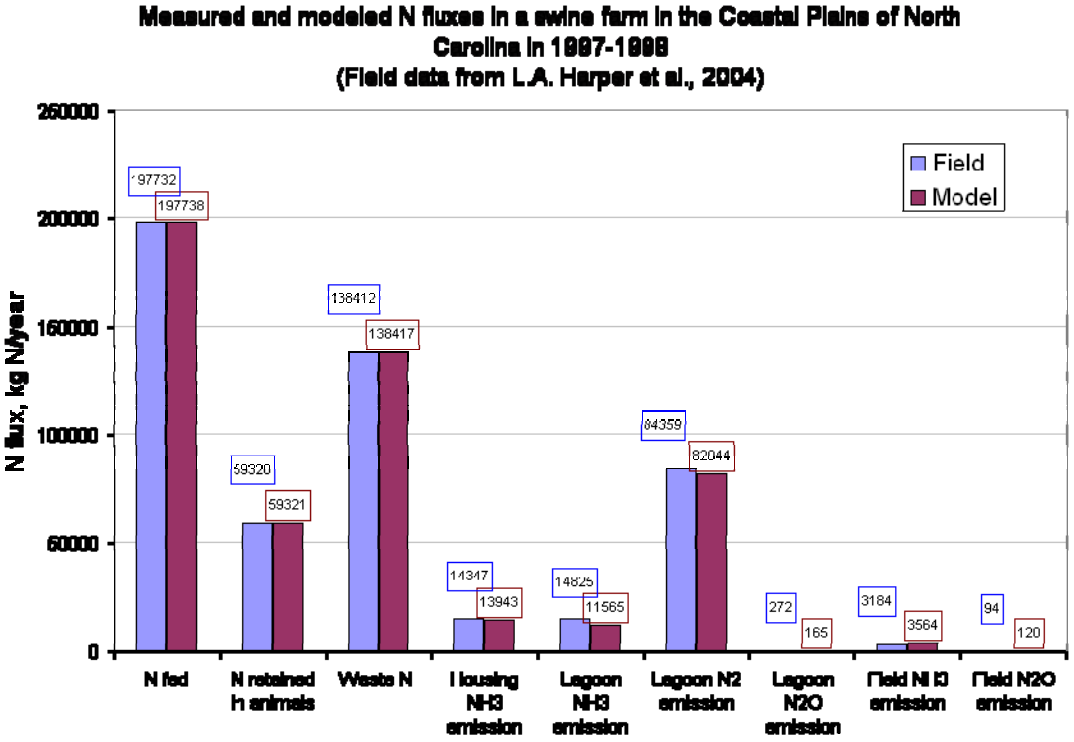


**Figure 19. Comparison between observed and modeled N fluxes for a swine farm in North Carolina.**

**Table 10. Measured and modeled N fluxes in a swine farm in North Carolina (unit kg N/year)**

| | Field | Model |
|---|---|---|
| N fed | 197732 | 197738 |
| N retained in animals | 59320 | 59321 |
| N in urine and dung | 138412 | 138417 |
| Housing NH3 emission | 14347 | 13943 |
| Lagoon NH3 emission | 14825 | 11565 |
| Lagoon N2 emission | 84359 | 82044 |
| Lagoon N2O emission | 272 | 165 |
| Field NH3 emission | 3184 | 3564 |
| Field N2O emission | 94 | 120 |

## 4.3. Manure-DNDC Model Simulations

In summary, for the entire simulation of the manure life cycle in a dairy farm, Manure-DNDC basically performs three key sets of calculations: (1) manure mass balance transfer through the farm components (e.g., feeding lots, storage/treatment facilities and field); (2) tracks dynamics of the environmental factors (e.g., temperature, moisture, pH, Eh and substrate concentration

gradients) in each of the farm components; and (3) simulates the rates of the biogeochemical processes (e.g., hydrolysis, decomposition, $NH_3$ volatilization, nitrification, denitrification, fermentation) occurring in each of the farm manure management components. The fluxes of $NH_3$, $CH_4$, $N_2O$ and $CO_2$ are the products of the modeled biogeochemical processes.

The overarching goal of this project was to develop Manure-DNDC as a generic model of C and N biogeochemistry for California dairies. However, we expect the model will be applicable to serve a wide range of animal farms in the U.S. Since the biogeochemical processes embedded in the model were adopted from the basic physical, chemical or biological laws which are based on first principles which and have been well documented in textbooks or other publications, if the environmental factors can be accurately tracked, the model should theoretically produce acceptable results. However, in consideration of the complexity of the animal farms in light of their varied sizes, animal types, and management precision and intensity, accurately predicting the environmental variables of animal farms would be one of the major efforts to improve the model performance in future.

### *4.3.1. Model Simulations*

While the current version of Manure-DNDC requires more validation before its emissions estimates can be considered with a known level of accuracy and uncertainty, the current version of Manure-DNDC was used to compile an initial estimate of $CH_4$ and $N_2O$ emissions from California dairies. The simulations were performed for each of the dairies where we had permit data describing manure management practices (e.g. frequency of dry lot scraping, land application, type and size of manure storage/treatment facilities, etc), type of dairy (freestall, corral, etc), number of cows (lactating, dry and heifers). There were 265 dairies for this analysis. These dairies had just over 1 million milking cows, which is approximately 56% of the total 1.8 million milking cows in the state. CIMIS climate data and SUSRGO soils data were used for the simulation. Without specific information on housing size, feed regimes, bedding, water used for flushing freestalls, size of corrals, etc, we had to make some simplifying assumptions. Table 11 provides a list of our assumptions and the basis for making each assumption.

**Table 11 Default input parameters for regional runs of Manure-DNDC.**

| Input | Default Value | Source |
|---|---|---|
| **Dairy Infrastructure and management** | | |
| Free Stall Barn size | 9.7 $m^2$/cow | SMP CA3B (Site Monitoring Plan for California NAEMS site). Free stall housed 600 cows in a 5,797 $m^2$ area, equivalent to 9.7 $m^2$ per cow. |
| Amount of flush water used per flush. | 76 liters/cow | Assume that lagoon water is recycled as flush water. Therefore, we assume that each time lagoon water is applied to land that an equivalent amount of fresh water |

| | | | |
|---|---|---|---|
| | | | will be used as flush water. |
| Initial bedding in Free Stalls at beginning of simulation | 45 kg/cow | | Rough estimate based on general volume of bedding material (needs refinement). |
| Size of corrals for drylot dairies and turnout areas | 42 $m^2$/cow | | Based on scale figure in SMP CA3B |
| **Feed** | Lactating | Dry Cows | |
| Dry Matter/day | 19.35kg | 11.61kg | UC DANR Committee of Experts on Dairy Manure Management Report, September 2003. |
| Carbon Intake/day | 7.74kg | 4.64kg | UC DANR Committee of Experts on Dairy Manure Management Report, September 2003. |
| Nitrogen Intake/day | 0.58kg | 0.35kg | UC DANR Committee of Experts on Dairy Manure Management Report, September 2003. |
| Protein Intake/day | 0.62kg | 0.37kg | UC DANR Committee of Experts on Dairy Manure Management Report, September 2003. |
| **Default Cropping System: Silage Corn** | | | |
| Planting Date | May 15th | | |
| Harvest Date | September 25th | | |
| Type of Fertilizer | 6-20-20 ($NH_4$+$PO_4$) and Anhydrous | | UCCE Silage Corn Cost Return Study (2001) |
| Fertilizer rates and application dates | 121 kg N/ha on May 15th, 66 kg N/ha on 6/15, 7/5, and 7/20 | | |
| Irrigation (amount and dates) | 8.21cm on 3/20 5cm on 6/1, 6/15, 7/5, 7/20, 8/1, 8/15, 8/25 and 9/5 | | UCCE Silage Corn Cost Study for amounts, dates were selected to spread the irrigation events throughout the growing season. |
| Tillage (dates and type) | Deep rip (20cm) on 4/15; Disc (10cm) on 4/16 and 9/30 | | UCCE Silage Corn Cost Return Study (2001), gives pre-plant and post harvest estimates of tillage. |

Since lactating and dry cows receive very different feed regimes and often have different manure management practices, we ran Manure-DNDC twice, once for lactating cows and once for dry cows, for each of the permit dairies. The 530 simulations (265 permits, with 2 simulations per facility) were then compiled in a spatial database to examine spatial and

temporal variability in emissions and to facilitate scaling emissions estimates up to the county and state level. We used the 2004 climate year for this simulation.

Based on the results from the permit dairy simulations, we scaled up the emissions to the statewide level by using average emissions at the county scale from our permit based model runs. For those counties that had dairies, but did not have dairies in our permit database, we used an average value from all the permit simulations. The Manure-DNDC based emission factors were then applied to each of our DWR dairy polygons throughout the state. Figure 20 shows the distribution of dairy cows (milking and replacement stock) from our databases (figure presents total number of cows – milking and replacement stock - across California in a 5km grid.

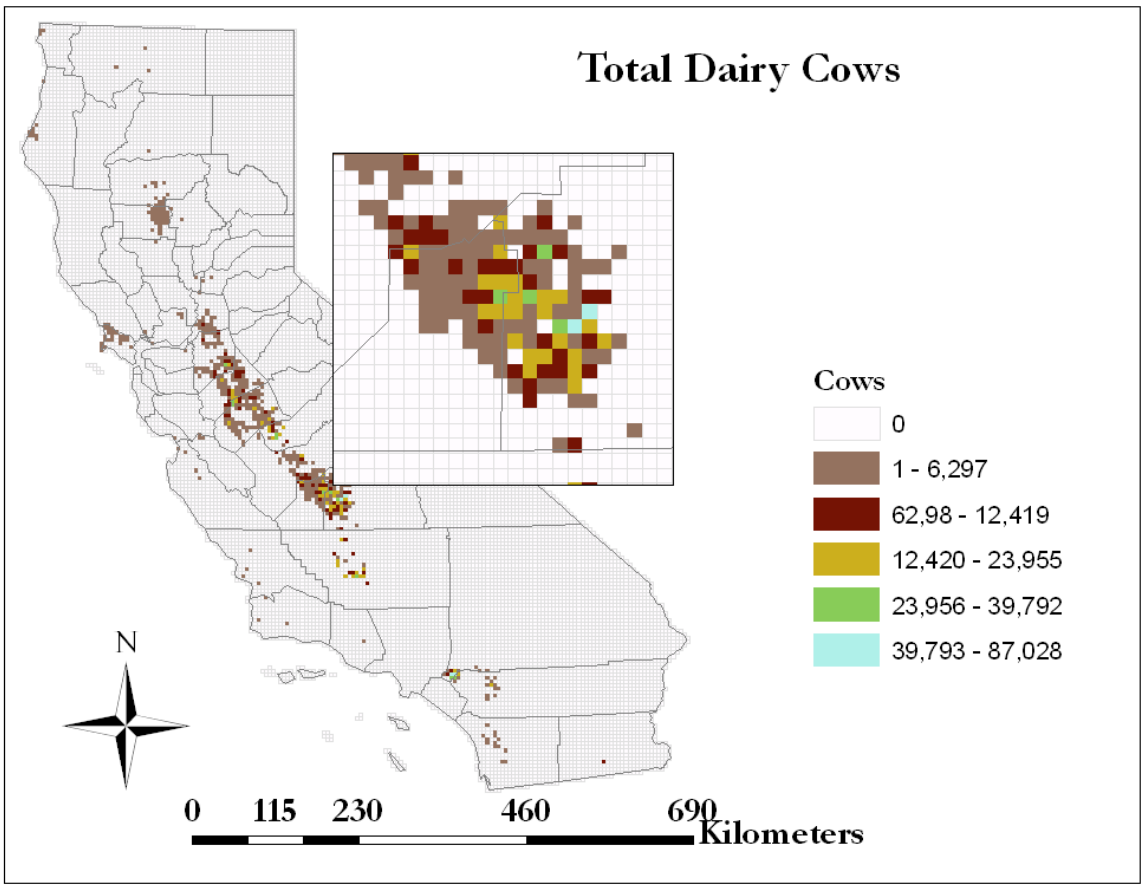


**Figure 20: Distribution of dairy cows in California. Our DWR location and cow population assignments were gridded to a 5km grid cell for illustration purposes. The number of cows includes both milking cows and their replacement stock (Heifers and Calves). It is clear that the bulk of dairy cows are in the central valley, with some pockets east of Los Angeles and north of San Francisco.**

### *Methane Emissions*

Our model results indicate that total methane emissions from dairies in 2004 was approximately 485,000 Metric Tons (MT). Following the IPCC Second Assessment Report guidance (SAR, 1996 vintage) using a GWP factor of 21 for $CH_4$, the methane emissions were 9.8 MMT (Million MT) $CO_2$eq. There were 3 main sources of methane emissions: enteric fermentation, lagoon/storage ponds, and compost piles. Enteric fermentation was the largest source of $CH_4$ emissions, accounting for approximately 83% (or 8.1 MMT $CO_2$eq.) of the total emissions. Lagoons/storage ponds accounted for 15%, or 1.6 MMT $CO_2$eq. Compost piles made a small contribution of approximately 1% (0.1 MMT$CO_2$eq.) of the total emissions. Our model estimate of total methane emissions is quite close to the 2004 CEC emission inventory estimate of 10.4 MMT $CO_2$eq. (CEC 2006). However, the estimates differ in the contributions from enteric and manure management. CEC (2006) estimates were 4.7 MMT $CO_2$eq and 5.7 MMT $CO_2$eq for enteric and manure management emissions, respectively.

### *Nitrous Oxide Emissions*

Our model results indicate that total nitrous oxide emissions from dairy manure management (includes emission from animals, housing, and manure storage/treatment) in 2004 was approximately 9,000 Metric Tons (MT). Following the IPCC Second Assessment Report guidance (SAR, 1996 vintage) using a GWP factor of 310 for $N_2O$, the nitrous oxide emissions were 2.8 MMT $CO_2$eq. Enteric (directly from the cows) and compost/solid stacks were the main sources of $N_2O$ emissions. The existence of direct $N_2O$ emissions from the cows themselves is a source of emissions that has not been accounted for in emission inventories. Our model estimates of enteric $N_2O$ emissions are based on the chamber work described above (Component 1). Our model estimate of total enteric $N_2O$ emissions is 0.8 MMT $CO_2$eq. If our estimates of direct emissions of $N_2O$ from dairy cows is accurate, then this is an important finding and needs to be addressed further. Compost was another source of $N_2O$, contributing 0.3 MMT $CO_2$eq. For comparison, the CEC 2004 estimate of $N_2O$ emissions from manure management is 0.9 MMT $CO_2$eq.

Manure-DNDC also provides estimates of $N_2O$ from land application phase of manure management. For these model runs we assumed that all manure effluent from lagoons and compost/solid stacks were applied to the surrounding crop areas. The extent of crop areas was taken from the permits (producers were asked how many acres of cropland they had and used for manure application). We also assumed that these surrounding crop areas were planted with a single corn silage crop. While most dairies grow several types of silage and forage crops, we decided to select a single crop for this demonstration. Manure-DNDC can simulate a wide variety of crops and cropping systems (including multi-cropping systems, use of cover crops, and a wide range of tillage, irrigation and fertilizer management systems). Total 2004 emissions from land application of manure and production of the silage corn, which includes the application of ~300 kg N/ha chemical fertilizer, was approximately 22,300 MT $N_2O$ (6.9 MMT $CO_2$eq.). The 2004 CEC emission inventory estimated total $N_2O$ emissions from agricultural soils was 19.2 MMT $CO_2$eq. Unfortunately it is not possible to directly compare the CEC emission estimate with our model results because the CEC estimates includes manure and chemical

fertilizer applied to all agricultural soils, while our estimate provides emission just from soils that received dairy manure.

Figure 21 illustrates the spatial pattern and magnitude of total $CH_4$ and $N_2O$ emissions, expressed as $CO_2eq$. As expected, high emissions are evident in areas with high density of dairy farms and cows. Figure 22 illustrates the difference between our total enteric emissions (methane and nitrous oxide) and the CEC (2006) estimate for 2004. Our estimate of total enteric emission is approximately 90% higher than the emission inventory estimate (Figure 22).

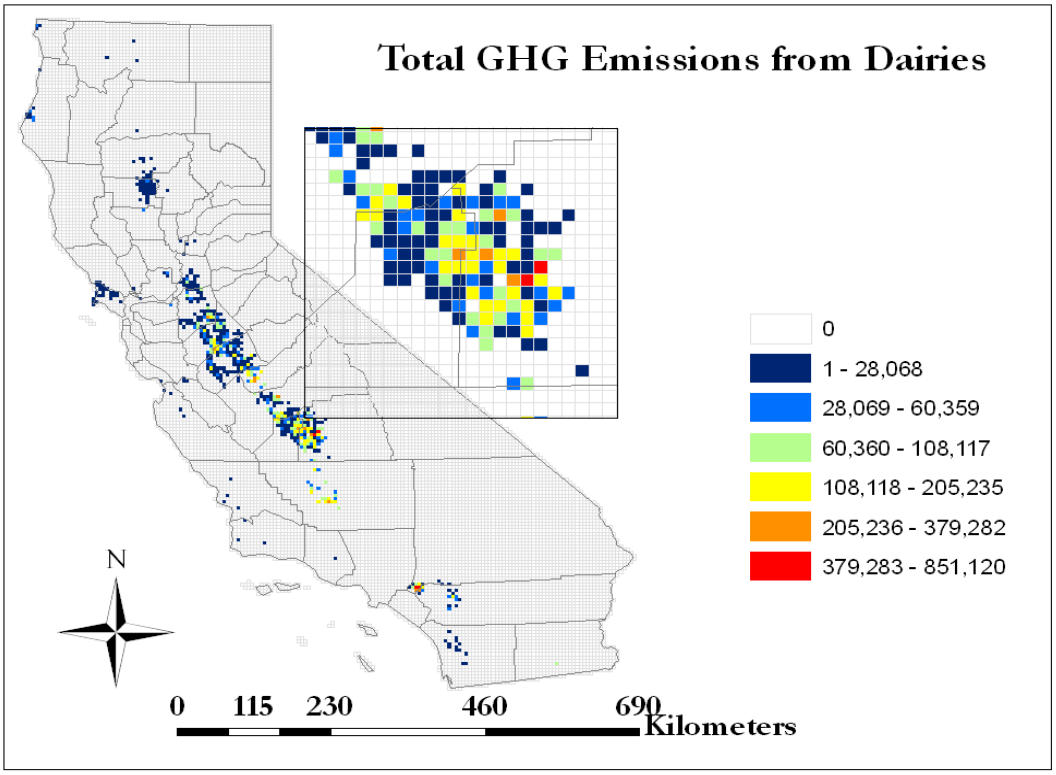


**Figure 21: Total methane and nitrous oxide emissions from California dairies. These model estimates include emissions from the dairy cows, manure management systems and land application. Note: the land application emissions also include emissions from cropping areas that received dairy manure. All dairy cropping areas were modeled as silage corn with ~300 kg N/ha of chemical fertilizer.**

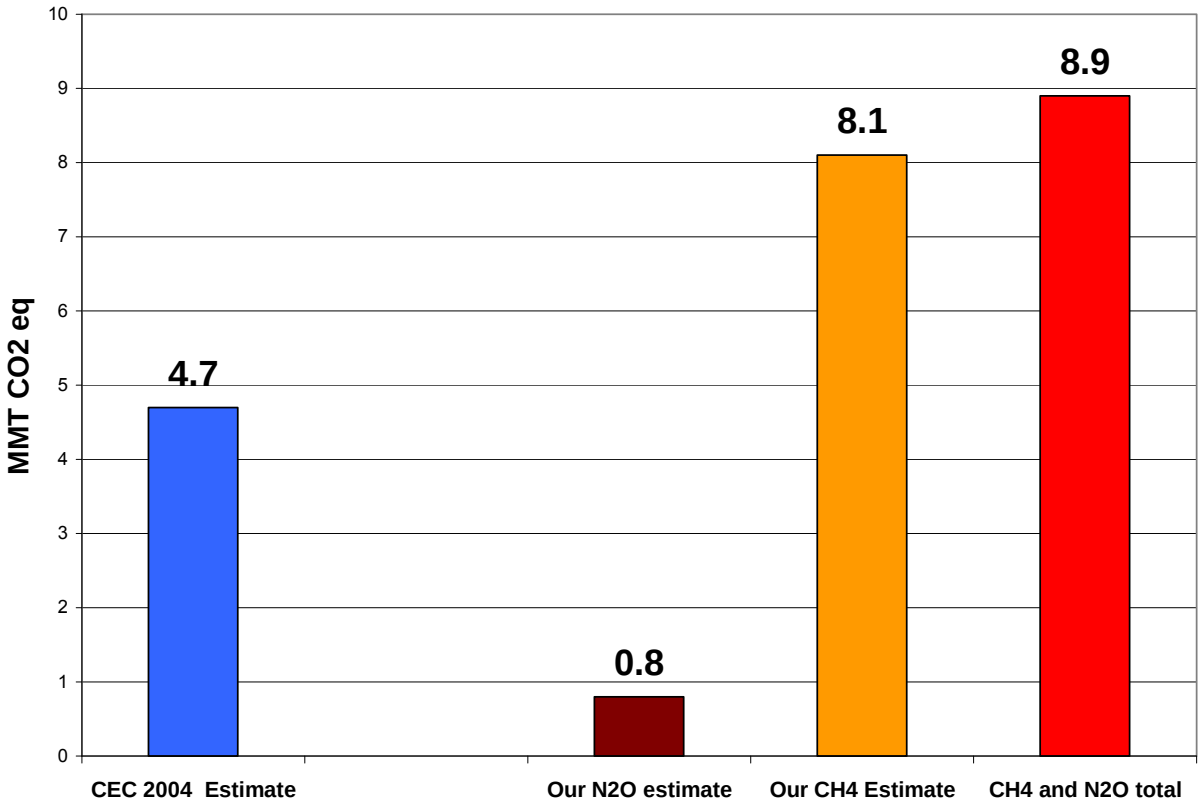


**Figure 22: Comparison of 2004 California Emission Inventory estimate of enteric fermentation emissions from dairy cows with our model estimates of enteric sources of methane and nitrous oxide.**

# 5.0 Overall Conclusions and Recommendations

The Environmental Chambers and the Cattle Pen Enclosures at UC Davis proved to be very useful for measuring greenhouse gases from enteric fermentation, fresh manure and standard housing conditions. Dairy farms may produce high fluxes of $CH_4$ (>12 g $cow^{-1}$ $h^{-1}$) from animals and their fresh manure. Enteric fermentation was the main process responsible for production of $CH_4$, while fresh manure did not produce noticeable fluxes. Lactating cows and their manure produced more $CH_4$ than dry cows and manure most likely due to the larger amount of fermentable substrate in both feed and feces. Future research needs to address the mitigation of $CH_4$ from cow digestive processes.

An FTIR system was developed to measure concurrently $N_2O$, $CO_2$, CO, $N_2O$, $CH_4$, $NH_3$, Hydrocarbon Concentrations. The data were used to make estimations of $N_2O$ flux from dairy dry lot using the flux gradient method. Typical $N_2O$ flux values from the dry lot over this study averaged around 25-30 ng/sec $m^2$, which is equivalent to an annual emission of 7.9 to 9.5 kg N2O/ha. Ambient $N_2O$ concentrations were observed to be elevated (>10%) just after a rain event, indicating the precipitation patterns may lead to significant temporal and spatial variability in dry lot nitrous oxide emissions. Ambient $N_2O$ concentrations were observed to be slightly higher above a compost pile than the dry lot. Concentration increased dramatically after the compost pile was disturbed. Due to the sensitivity to micro-meteorological conditions and difficulty in estimating exactly the area of emission source, the FTIR approach for $N_2O$ data collecting for model validation is lacking. Future data collection will focus on the use of flux chambers.

In addition, through the funding from this CEC project, we were able to get funding the the CSU ARI program to fund additional N2O emission measurements using flux chambers and an INNOVA Acoustic Analyzer. These data are being collected in 2007 and 2008 and will be used for model validation in late 2008 to early 2009. These chamber measurements will be better than our FTIR results for understanding of the spatial and temporal variability of $N_2O$ emission from drylots and would improve the utility of the data for validating process models.

The modeling component of this project achieved it main goals of designing and building a process-based modeling tool for estimating GHG emissions from individual dairies or regions with dairies, developing and testing FTIR approaches for measuring $N_2O$ emissions from components of dairies, collecting new emissions data in controlled chambers to improve our understanding of enteric sources of GHG emissions, and building spatial databases for regional model simulations. This modeling effort is attracting more interest and support from the dairy industry, which has funded a project to extend the model to dairies throughout the country and to include VOCs and Hydrogen Sulfide gases. We expect Manure-DNDC will become a useful tool for livestock industry in the coming years after the thorough calibration and validation activities planned for 2008. Further research is needed to perform more extensive model validation to improve our understanding of the accuracy and uncertainties of model estimates. We recommend the following next steps:

- Collect additional GHG emission data specifically for model validation. Data should be collected using automated chambers (to capture the episodic nature of $N_2O$ emissions). Chamber data can be used to assess the efficacy of using open path FTIR technology for area emission estimates.
- Perform additional studies on $N_2O$ emissions directly from dairy cows, including testing various feed regimes impact on emissions.
- Transition the modeling and GIS databases from a research tool to an easy to use decision support system for comprehensive assessment of dairy management impacts on local air quality, water quality and greenhouse gas emissions. Manure-DNDC is designed for detailed biogeochemical modeling with the flexibility to examine and prioritize a suite of management alternatives for mitigating greenhouse gas emissions.

This project has accomplished it objectives to develop a modeling tool for greenhouse gas emissions from dairies. However, we recognize that this work is far from complete and we expect this modeling tool to evolve and improve with more experiments and validation efforts. California will benefit from this project through an improved understanding of greenhouse gas emissions from dairies and availability of a sophisticated modeling tools for improving emissions inventories and evaluation of potential mitigation strategies to reduce the greenhouse gas footprint of dairies in the State.

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# 7.0 Glossary

| | |
|---|---|
| AB | Assembly Bill |
| ADG | Average Daily Gain |
| ATV | All-Terrain Vehicle |
| BGT | Black Globe Temperature |
| BW | Body Weight |
| CARB | California Air Resources Board |
| CDFA | California Department of Food and Agriculture |
| $CH_4$ | Methane |
| CIMIS | California Irrigation Management Information System |
| CON | Control |
| $CO_2$ | Carbon Dioxide |
| CPE | Cattle Pen Enclosure |
| DM | Dry Matter |
| DMI | Dry Matter Intake |
| DNDC | DeNitrification-DeComposition model |
| DWR | Depart of Water Resources |
| GC | Gas Chromatography |
| GHG | Greenhouse Gas |
| GWP | Global Warming Potential |
| HAR | Harrowing |
| NAAQS | National Ambient Air Quality Standards |
| NASS | National Agriculture Statistics Service |
| $NH_3$ | Ammonia |
| NOx | Oxides of Nitrogen |
| $N_2O$ | Nitrous Oxide |
| OFP | Ozone Forming Potential |
| PAS | Photoacoustic Spectroscopy |

| | |
|---|---|
| SBS | Sodium Bisulfate |
| SCR | Scraping |
| SJV | San Joaquin Valley |
| SJVAPCD | San Joaquin Valley Air Pollution Control District |
| TMR | Total Mixed Ration |
| USDA | United States Department of Agriculture |
| VFA | Volatile Fatty Acid |
| VMTH | Veterinary Medical Teaching Hospital |
| VOC | Volatile Organic Compound |

# APPENDICES

Appendix A: Contains detailed information on the biogeochemistry in the Manure-DNDC model. It includes a table of equations.

Appendix B: Contains information on the FTIR testing, design and setup at the CSUF dairy.

# Appendix A: Manure-DNDC Biogeochemical Processes

## Biogeochemical processes in feeding lot

Feeding lots including house, outdoor pen and grazing pasture, are the place where manure is originally produced through excretion of the animals. Defining the quantity and quality of the manure at its beginning is crucial for the entire manure life cycle simulation. The quantity and quality of fresh manure in a farm depend on a number of factors such as the animal type, animal physiological status, herd size, feed materials etc. Manure-DNDC acquires the input information by reading a special input file prepared in advance. The input file consists of the animal type, animal population, feed rate and crude protein content data at daily time step for a year or a selected time span. The animal types simulated by Manure-DNDC are classified into dairy cow, beef cow, veal, swine, sheep, goat, horse, layer, broiler, turkey and duck. In consideration of the variability and complexity of feed materials, the quantity and quality of the feed materials are generalized into two parameters, i.e., feed rate in dry matter per animal per day and crude protein (CP) content in feed. During the simulation, Manure-DNDC first calculates daily feed N amount based on the animal type, feed rate and feed CP concentration (Equation 1 in Table A-1). The modeled feed N is then partitioned into milk, meat and excreta based the proportions reported by Powel et al. (2006) and other researchers. According to Broderick (2003) and Wattiaux and Karg (2004), the excreta N is equally split to feces and urine. Based on the reported C/N ratio values in feces and urine, the C contents in feces and urine can be calculated. The C existing in feces is in form of manure solid; and the C in urine is in form of dissolved organic carbon (DOC). Water content in fresh manure is calculated based on observed feces moisture or urine production. As soon as the quantity and quality of the feces and urine are defined in terms of their C, N and water contents, the manure in both solid and liquid phases will be partitioned into the manure organic matter (MOM) accumulated on the floor of the feeding lot. For outdoor pen or grazing plot, the feces and urine will be mixed and jointly added into the MOM. For the houses where the solid and liquid wastes are separated with the facilities such as slatted floor with under-floor gutter, the majority of urine will be stored in the gutter and solids stay on the floor.

Hydrolysis: As the liquid part of manure, urine contains N mainly in form of urea. No matter the urine is located into the MOM or gutter slurry, the urea in the urine will undergo the first biogeochemical reaction, hydrolysis. The N existing in urine is mainly in the form of urea ($CO(NH_2)_2$), which is subject to hydrolysis to convert to $NH_4^+$:

$$CO(NH_2)_2 + 3H_2O = 2NH_4^+ + HCO_3^- + OH^-. \quad (1)$$

In manure, urease plays a key role in hydrolysis of urea. Urease activity is mainly regulated by soil organic carbon (SOC) contents (Zantua and Bremner, 1976; Paulson and Kurtz, 1969; Myers and McGarity, 1968; Gould et al., 1973; and Fenn et al., 1984), moisture (Fenn et al., 1981; Fox and Hoffman, 1981; Matocha, 1976), and temperature (Gould et al., 1973; Fisher and Parks, 1958). In Manure-DNDC, the urease activity is calculated as a function linearly related to the DOC content, moisture, and temperature in the manure; and daily hydrolysis rate is a first

order of the urease activity and urea (Equation 2 and 3 in Table A-1). During the urea hydrolysis, more OH- is introduced into the manure system that will elevate the manure pH.

Decomposition: In parallel with the urea hydrolysis, the manure solids allocated in the MOM first undergo decomposition. In Manure-DNDC, MOM consists of four organic carbon pools, namely residue litter, living microbial biomass, humads (i.e., active humus) and passive humus. Each of the pools has labile and resistant fractions. Decomposition (as modeled in Manure-DNDC) can simultaneously occur in the first three organic matter pools (i.e., decomposable residues, microbial biomass and humads). The passive organic phase is assumed to decompose very slowly. The initial partitioning of fresh manure into the MOM pools is determined based on C/N ratio of the manure solids (Equation 4 in Table A-1). Each of the MOM pools has a specific decomposition rates subject the manure temperature and moisture. The specific decomposition rates are listed in Equation 5 in Table A-1). During the decomposition process each pool decomposes independently. The relationship of the pools is shown in Figure A-1. The MOM carbon pools (residue litter, humads and humus) decompose via first-order kinetics. This formulation has been widely used to estimate mineralization potentials of soil organic carbon (SOC), and yields results consistent with data from incubation studies (Molina et al 1983; Stanford and Smith 1972; Smith et al 1980; Deans et al 1983; El-Haris et al 1983; Deans et al 1986). Since there is a significant difference in the C:N ratio between residues and microbial biomass (Equation 5 in Table A-1), the actual decomposition rates for residues are affected by the availability of nitrogen in the soil. A reduction factor is introduced into the decomposition equation to reflect the limitations set by available N (Li et al., 1992). Bedding practices could affect decomposition of the manure accumulated on the floor of feeding lots. Adding straw or sawdust, which usually has high C/N ratio, will elevate the manure C/N ratio and reduce decomposition rate; adding mineral solids containing clay will decrease decomposition rate as clays can adsorb organic C and shelter it from decomposition (Bouwman 1990). Vertisols (see USDA 1975; FAO/Unesco 1972) showed a linear relationship between soil carbon and clay content between 35 and 80% clay. As the residue litter pools decompose, the carbon released is either respired as $CO_2$ or incorporated into microbial biomass in the manure (see Figure A-1). Manure-DNDC first determines the amount of $CO_2$ produced by litter decomposition and, from this and a microbial efficiency, calculates the amount of carbon incorporated into microbial biomass, with 90% going into labile biomass and 10% going into resistant biomass (Gilmour et al 1985). Microbial efficiency, defined here as the ratio of C assimilated into microbial biomass to residue C released by decomposition, has been reported to vary between 20% and 60% (Paul and Juma 1981; Paul and Van Veen 1978; Chichester et al 1975; Molina et al 1983; Gilmour et al 1985). In the manure rich in easily decomposable organic material, the microbial population buildup is high (Griffin and Laine 1983). In Manure-DNDC, the efficiency values of 60% for manure is adopted. As microbes die and their biomass decomposes (see Figure A-1) 20% of the carbon is transferred to $CO_2$, sixty percent of the carbon is re-incorporated into new microbial biomass and 20% is transferred to the resistant humads pool (Molina et al 1983; Gilmour et al 1985). The resistant humads pool can lose carbon through decomposition. As each humads pool decomposes, 40% of the carbon is transferred to the resistant humus pool, 40% of the carbon is converted to $CO_2$ and 20% of is re-incorporated into microbial biomass (Molina et al

1983). Physical disturbance of the manure will increase decomposition rates for all the MOM pools. The dissolved organic carbon (DOC) pool (see Figure A-1) consists of the carbon from microbial biomass decomposition (60%) and humads decomposition (20%) that is recycled into microbial biomass.

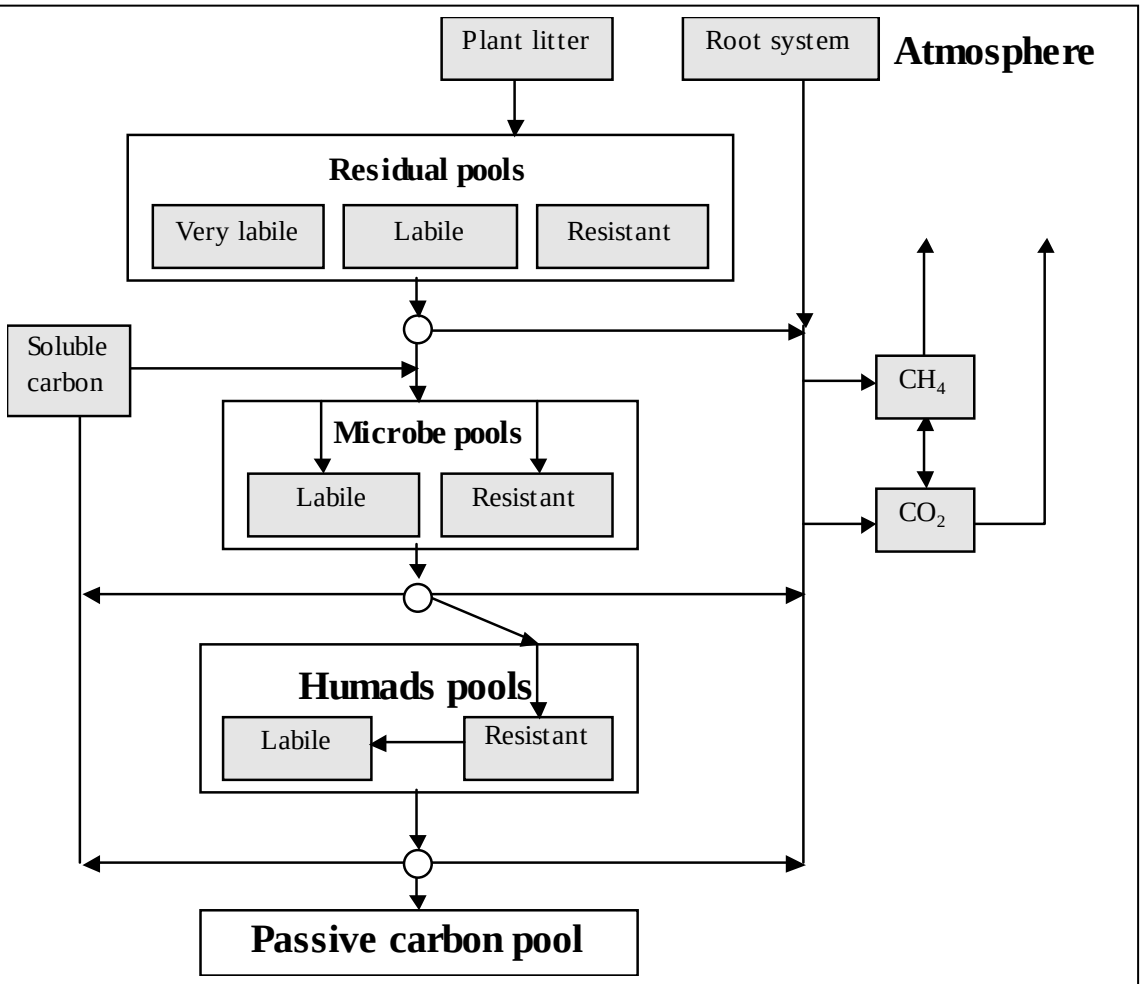


**Figure A-1. Major carbon pools and fluxes of manure modeled in Manure-DNDC**

Both the manure temperature and water content affect the decomposers' activity (Alexander 1971), and this effect is modeled by reduction factors which reduce the decomposition rate for non-optimum conditions. The effect of temperature and moisture on microbial activity used in Manure-DNDC is taken from Nyhan (1976) and Clay et al (1985). These relationships between microbial activity and both temperature and moisture are generally consistent with the results of other studies (e.g. Bremner and Shaw 1958a,b; Witkamp 1966; Alexander 1971; Meyers and McGarity 1971; Jager and Bruins 1974; Wildung et al 1975). Since the reduction factor

represents the combined effect of the temperature and moisture reduction factors, it is taken as the product of the two factors.

Ammonia volatilization: During the decomposition processes, when organic C is oxidized to CO2, part of the associated N is transformed to ammonium (NH4+) (LI et al., 1992). The NH4+ dissolved in the manure liquid phase keeps in equilibrium with the dissolved ammonia.

NH4+ = NH3(l) + H+.

The equilibrium is subject to the manure pH, temperature, NH4+ concentration and NH3 concentration. The NH4+/NH3 equilibrium constant (Ka) and water dissociation constant (Kw) are strongly temperature-dependent. Following the calculations used by Glasstone (1946), Stewart et al. (1977), and Sutton et al. (1993), we integrate the relationships among the factors into a group of equations listed in Equation 6 in Table A-1. Manure calculates NH3 volatilization flux a function of NH3 concentration in the liquid phase and manure temperature and moisture (Equation 7 in Table A-1). During the processes leading to NH3 volatilization, the manure system gains proton (H+) that will lead to decrease in the manure pH.

Clay adsorption of ammonium: If clay minerals or other absorbents exist in the manure due to bedding or manure mixture with the ground soil in feeding lot, Manure-DNDC will partition NH4+ between the clay-adsorbed NH4+ phase and free NH4+ phase based on the clay content and total NH4+ concentration in the manure soil (Equation 8 in Table A-1). When leaching water pass the manure, the adsorbed NH4+ can be released based on the adsorption/disorption processes.

Nitrification: The NH4+ existing in manure can be oxidized to NO3- through a microbially mediated reaction, nitrification (McGill et al 1981; Van Veen & Frissel 1979).

NH4+ + O2 -> NO3- + H2O.

According to a study by Watts and Hanks (1978) and Hadas et al. (1986), the potential rate of nitrification in soil is related to the available NH4+, temperature and moisture. In Manure-DNDC, the activity of nitrifiers is determined by NH4+ concentration, temperature, moisture, pH, Eh, and total organic carbon content in the manure (Equation 9 in Table A-1). During nitrification, a certain amount of N2O or NO can be evolved

(Bremner and Blackmer 1978). The amount of emitted N2O correlates with the amount of nitrifiable N (e.g. Parton et al 1988). In Manure-DNDC, the N2O or NO emission from nitrification is calculated as a constant fraction of nitrification rate based on Bremner and Blackmer (1981).

Denitrification: When the manure Eh slightly decreases due to moisture increase or oxygen depletion by the manure microbes, the nitrate (NO3-) existing in the manure could be reduced to nitrite (NO2-), nitrous oxide (N2O), nitric oxide (NO) and finally dinitrogen (N2) by a group of the manure microbes. The sequential reactions are called as denitrification.

$NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$.

It is crucial for predicting nitrification to quantify the manure Eh dynamics. In Manure-DNDC, the Nernst equation and the Michaelis-Menten equation have been integrated to track the evolution of manure Eh as well the microbial activities in the manure. A computing scheme, "anaerobic balloon", was adopted in Manure-DNDC to realize the integration of the two equations in the modeling framework. The anaerobic balloon is defined as the volumetric fraction of anaerobic micro-sites in manure. The size of the balloon varies between 0 and 1 representing fully aerobic and anaerobic conditions, respectively. With the Nernst equation, Manure-DNDC calculates manure Eh based on concentrations of oxygen, nitrate or other dominant electron acceptors in the manure. And then the size of the anaerobic balloon is defined based on the modeled Eh. It is defined that the micro-sites within the balloon are anaerobic, and that outside the balloon are aerobic. The substrates (e.g., DOC, ammonium, nitrate etc.) will be then proportionally allocated into the aerobic and anaerobic fractions. It is defined that only the substrates allocated in the aerobic fraction will participate in the oxidative reactions (e.g., nitrification); and the substrates allocated in the anaerobic fraction will participate in the reductive reactions (e.g., denitrification). Given the substrate contents partitioned into the aerobic and anaerobic micro-sites, rates of the relevant oxidative and reductive reactions will be calculated based on the Michaelis-Menten equation. Based on the modeled consumption rates of the substrates involved in the redox reactions, Manure-DNDC will reestablish the substrate concentrations and the new Eh value. Through the computing loop of "Eh definition-substrate allocation-microbial activity-substrate consumption-Eh change", Manure-DNDC tracks dynamics of soil Eh as well microbial activity to quantify the production and consumption of greenhouse gases at hourly or daily time step. Manure-DNDC simulates the anaerobic balloon driven by oxygen and other oxidants (Equation 13 in Table A-1). If manure is fully aerobic (Eh > 350 mV), $O_2$ will be used as the dominant electron acceptor by the manure microbes. In the case, $CO_2$ is the major gas produced in the manure. If the manure moisture increases due to urine excretion, watering or rainfall event, the manure $O_2$ can be gradually depleted to drive the oxygen-driven anaerobic balloon to swell. When the manure $O_2$ is depleted, the oxygen-driven balloon will reach its maximum and burst, and then a new balloon will appear driven by the next electron acceptor, nitrate. Within the nitrate-driven anaerobic balloon, denitrification will occur to produce nitrite, NO, $N_2O$ and $N_2$ sequentially.

Manure-DNDC calculates denitrification processes by tracking denitrifiers growth rate, death rate, nitrogen oxides consumption, and N gases emissions in manure. Almost all denitrifiers are capable of anaerobic growth only in the presence of $NO_3^-$, $NO_2^-$, or $N_2O$. The growth rates of denitrifiers directly affect the reduction rates of these nitrogenous oxides. Denitrifiers are assumed to become active at the onset of a depression of the manure Eh. A short (1 to 10 hour) lag period before denitrification began following manure wetting (Tiedje, 1978; Smith and Tiedje, 1979). The growth rates of the bacteria are taken to be proportional to their respective amounts of biomass (van Veen and Frissel 1981). Relative growth rates, which depend on the concentrations of DOC and electron acceptors (N-oxides), can be calculated with double-Monod kinetics, a simple function describing multiple-nutrient-dependent Michaelis-Menten type growth (Bader 1978). Following Leffelaar and Wessel (1988), we assume that the relative

growth rates for denitrifiers with different substrates are independent; competition among the bacteria takes place via the common soluble carbon substrate (Equation 10a in Table A-1). Denitrifiers growth rate is affected by temperature and pH. An exponential relationship between denitrification rate and temperature has been observed by many researchers (e.g., Focht 1974; Nommik 1956; Dawson and Murphy 1972). According to Bailey and Beauchamp (1973) and Nommik (1956), the rate of denitrification is very temperature-dependent in the 10-35°C range, with a Q10 near 2.0 (Stanford et al 1975a; Knowles 1981). The rate continues to increase at higher temperatures, reaching a maximum at 60-75°C and then falling to zero at higher temperatures (Keeney et al 1979; Bremner and Shaw 1958b). At lower temperatures the denitrification rate decreases but is measurable down to 0-5°C (Bailey and Beauchamp 1973; Bremner and Shaw 1958b; Smid and Beauchamp 1976). Since most parameters adopted in this study are based on a standard temperature of 22.5°C, the temperature effect factor is a standard exponential function (Q10 = 2) equal to 1.0 at 22.5°C. This one temperature factor is applied to the activities of NO3-, NO2-, and N2O denitrifiers. According to the experimental studies conducted for soils by Focht (1974) and Leffelaar and Wessel (1988), pH affects nitrate and nitrous oxide rates differently, such that, at low pH (<5), most denitrification stops at N2O. In general, total denitrification decreases as pH decreases.

The denitrifier death rate is modeled as proportional to denitrifier biomass. The C and N from dead cells are added to the pools of immobilized C and N and no longer participate in the dynamic processes (Leffelaar and Wessel 1988). Since denitrifier biomass is a very small fraction of total manure microbial biomass, this represents an insignificant loss of C and N from the manure system (Equation 10b in Table A-1).

During denitrification, DOC is used by bacteria as the basic material for cell synthesis and energy. The consumption rate of DOC depends on the biomass, relative growth rate, and maintenance coefficients of the denitrifier populations (Equation 10c in Table A-1). Nitrate, nitrite and N2O consumption rates are calculated with Pirt's equation (Equation 10d in Table A-1). According to Leffelaar and Wessel (1988), the maintenance coefficients (MNxOy) in Equation 10d must multiplied by the relative presence of each electron acceptor in the water phase (NxOy/N), because maintenance data reported in the literature for each reducing step are for maintenance sufficient to support the entire denitrifier biomass (NO3- denitrifier + NO2- denitrifier + N2O denitrifier). Based on the growth rates of denitrifiers and the C:N ratio in the bacteria, the assimilation of N during denitrification can be calculated (Equation 10e in Table A-1). A C:N ratio (by weight) of 3.45 is used, based on the chemical composition of denitrifiers ($C_6H_{10.8}N_{1.5}O_{2.9}$), in accordance with data reported for Paracoccus denitrificans (Verseveld and Stouthamer 1978).

The nitrification- or denitrification-induced N2O can be emitted into the atmosphere through diffusion. A highly simplified function built in Manure-DNDC to estimate the emitted N2O or N2 as a fraction of total N2O or N2 proportional to the air-filled porosity of the manure (Equation 10f in Table A-1). These emission factors are not gradient driven, and will undoubtedly create some artifacts in the shape of the denitrification N2O pulse.

Fermentation: When manure is under deeply anaerobic conditions, fermentation can occur, which produces methane (CH4) by oxidizing the C in DOC or CO2 with organic compounds as electron acceptors. As the terminal product of anaerobic decomposition of organic matter, CH4 could be emitted from the slurry in gutter or lagoon or the manure solids saturated with water or urine in feeding lot, compost or field. Manure-DNDC tracks Eh evolution in manure based on the above-described "anaerobic balloon". If the Eh is lower than -150 mv, CH4 production will be activated. As main energy source for the methanogens, CO2 and DOC are quantified in Manure-DNDC by tracking decomposition at daily time step. Manure-DNDC calculates CH4 production based on DOC, CO2, temperature, Eh, and pH (Equation 11a in Table A-1). In the manure, when the CH4 produced at the anaerobic microsites diffused to the microsites which processes relatively high Eh, the CH4 can be oxidized:

$$CH4 + 2O2 \rightarrow CO2 + 2H2O .$$

In Manure-DNDC, CH4 oxidation rate is regulated by CH4 concentration and the balk Eh of manure (Equation 11b in Table A-1). A simplified equation has been adopted in Manure-DNDC to estimate CH4 diffusion within manure based on its concentration gradients, temperature and air-filled porosity (Equation 11c in Table A-1).

Temperature and moisture are two key environmental factors affecting all the biogeochemical processes. Routines have been developed in Manure-DNDC to track the dynamics of manure temperature and moisture under the housing, outdoor pen or grazing field conditions. Manure-DNDC estimates house temperature based on the air temperature and ventilation rate (cubic m/sec) (Equation 12 in Table A-1). For outdoor pen and grazing pasture, the manure temperature is equal to the air temperature. Manure moisture is calculated based on the initial manure water content, evaporation, and water supplement or precipitation. Daily potential evaporation is determined with the Thornthwaite equation subject to wind speed or ventilation rate.

In Manure-DNDC, manure is defined as the combination of ten organic pools (i.e., very labile litter, labile litter, resistant litter, labile microbes, resistant microbes, labile humads, resistant humads, passive humus, urea and DOC) plus a series of inorganic pools of NH4+, NO3-, NO2-, N2O, NO, N2, NH3 and water. The quantity of manure is the sum of the C and N in all the organic and inorganic pools; the quality of manure is defined by the proportions of the pools. Through the above-described biogeochemical processes of decomposition, nitrification, denitrification, fermentation etc., the manure staying in the feeding lots changes in its not only quality but also quantity as part of the organic matter has been become CO2, CH4, NH3, N2O, NO and N2 emitted into the atmosphere while part of C and N transferred from the labile to the resistant pools. By tracking the mass balance for each of the simulated biogeochemical processes, Manure-DNDC precisely defines the new composition of the residue manure when it is released from the feeding lots. So when the manure is transported from the feeding lots to the storage or treatment facilities (e.g., compost, lagoon or anaerobic digester), the quantity and quality of the residue manure has been determined with all the organic and inorganic pools.

## Biogeochemical Processes in Manure Storage/Treatment

In Manure-DNDC, when manure is transported from feeding lot to compost, lagoon or anaerobic digester, actually the entire matrix of organic and inorganic pools are allocated in the storage or treatment facility. In the storage or treatment facilities, the same group of biogeochemical reactions will occur although under different environmental conditions.

For the compost component, the manure temperature is calculated based on decomposition rate and heat transmission. According to extensive field research, the heat value of manure on a dry ash free basis is estimated at 19.8 MJ/kg (Texas Cooperative Extension, The Texas A&M University System, E428, 11/06). In the early stage of composting, the DOC and labile organic carbon of manure decompose fast and generate a lot of heat to elevate temperature in the compost. The daily change in temperature is calculated based on the heat generation rate in the heat loss rate from the compost. The heat exchange rate between the compost and the surrounding air is a function of the temperature gradient between the compost and air as well the coverage of the compost (Equation 14 in Table A-1). For the lagoon component, the slurry temperature profile is estimated based on the air temperature, the lagoon slurry depth and the lagoon surface coverage (Equation 15 in Table A-1). The temperature in anaerobic digester is defined by the engineering specifications of the facility.

The moisture in compost is calculated based on evaporation rate and water addition through watering or precipitation. The evaporation rate is regulated by the compost temperature, density and coverage. The moisture in digester is kept constant as a parameter of the facility specifications.

Eh dynamics is tracked for compost, lagoon or digester by Manure-DNDC tracking oxygen consumption due to decomposition and oxygen diffusion from the atmosphere.

When the environmental factors (e.g., temperature, moisture, pH and Eh) are defined for each of the storage or treatment components, all the biogeochemical processes described in Table A-1 will be applied for the manure stored in compost, lagoon or anaerobic digester. Through the simulations for decomposition, nitrification, denitrifiaction, NH3 volatilization, fermentation etc., the fluxes of NH3, CH4, N2O, NO, N2 and CO2 emitted from the storage/ treatment facilities will be quantified, and the manure composition will be redefined.

When Eh becomes lower than -350 mV in compost, lagoon or digester, CH4 production will occur. The CH4 produced in lagoon can be emitted through bubble ebullition and diffusion. The ebullition rate is defined as a function of slurry temperature and CH4 concentration (Equation 16 in Table A-1).

In the lagoon component, nitrification is depressed due to the low Eh. The NH4+ from urea hydrolysis of MOM decomposition will continuously transfer to NH3 through the chemical equilibrium between NH4+ and NH3 in the liquid phase. A two-film module was adopted in Manure-DNDC to quantify NH3 emissions from the lagoon surface (Equation 17a,b,c,d in Table

A-1). The module first simulates the transport of NH4+ and NH3 from the bulk liquid to the interface, and then calculate NH3 transfer from the interface liquid phase to the interface gas phase before NH3 emitted into the air.

Anaerobic digesters have been widely utilized in animal farms for converting the waste to energy source (i.e., CH4). Manure-DNDC simulates anaerobic digestion based on the waste quantity/quality as well the facility specifications including capacity, treatment temperature and duration, and designed CH4 productivity. Under the anaerobic decomposition processes in high temperature, the litter, humads and humus pools of manure decompose to produce DOC, and the DOC will be utilized by the methanogens in the digester to produce CH4 (Equation 18 in Table A-1). Most the inorganic N released from the decomposition will remain in from of NH4+.

The initial pH of manure slightly varies between 6.9 and 8.1 depending on the animal type. When the manure stays in the storage/treatment facilities, the biogeochemical processes such as urea hydrolysis and NH4+/NH3 transformation can alter the manure pH by consuming or releasing H+ (Equations 3 and 4 in Table A-1). Manure Eh is mainly controlled by the oxygen concentration in compost. In lagoon or anaerobic digester, manure Eh is affected by more electron acceptors such as Mn4+, Fe3+, sulfate and DOC. Manure-DNDC tracks oxidants consumption during the reductive biogeochemical processes to track the Eh evolution (see details in Li, 2007).

The residue manure discharged from compost, lagoon or digester is partitioned for field application in the farm or for market for sale based on user-defined proportions.

## Biogeochemical Processes in Manure Field Application

Field application is an important part of manure life cycle, which partitions a big portion of the manure organic C and N into the soil organic pools while converts a significant manure N into crop biomass that could be used as forage for the farm animals and hence close the manure life cycle within the farm scope. Differing from the feeding lots or storage/ treatment facilities, the fate of manure applied in the field will undergo more complex processes which are affected by climate events, soil properties, crop growth and various cropping practices (e.g., tillage, fertilization, irrigation, grazing etc.). As soon as manure is applied in the field, Manure-DNDC will allocate all the organic and inorganic pools of the manure organic matter (MOM) into the corresponding pools of the soil organic matter (SOM). If slurry is applied, Manure-DNDC will simulate the slurry application as an event combining irrigation, organic matter amendment and urea application. The contents of water, organic matter and inorganic N in the slurry are determined based on the processes modeled in the lagoon component. Total thickness of a modeled soil profile is typically 50 cm since most biogeochemical processes mostly occur within the top 30-75 cm for most mineral soils (Gilliam et al 1978; Rolston et al 1976; Khan and Moore 1968). Initially, the top 10 cm of soil is assumed to be chemically uniform. Below this level, the concentrations of organic residues, organic C and NO3- decrease exponentially with depth (50% every 10 cm).

Plant N uptake is a major driver for the manure-induced N in the field. A routine was adopted in Manure-DNDC to simulate the crop growth. As plants grow they take up nitrogen in the form of nitrate or ammonium. Based on average rates of accumulation of nitrogen in aboveground crops (Olson 1978; Olson and Kurtz 1982), the daily uptake of N by crops is estimated according to crop type and plant growing stage. The plant nitrogen comes from NO3- and NH4+ pools, based on their proportions of the total free inorganic N pool (NO3- + NH4+). Daily transpiration and evaporation are calculated to track the soil moisture. If water stress occurs, the crop growth will be depressed. Common cropping practices such as tillage, irrigation, fertilization, grazing etc. have been parameterized in Manure-DNDC to quantify their impacts on the SOM dynamics.

Manure-DNDC simulates atmospheric NH3 deposition, i.e., atmospheric NH3 absorption by plants. The rates of NH3 absorption by plants is regulated by (1) NH3 concentration in the air around leaves (e.g. Hutchinson, 1972; Hutchinson et al., 1972; Meyer, 1973; Farquhar et al., 1980; Lockyer and Whitehead, 1986); (2) N shortage in crops (Harper et al., 1987), (3) leaf surface moisture (Dabney and Bouldin, 1985; Harper et al., 1987; Sutton et al., 1993), and (4) plant growing stage (Farquhar et al., 1979; Hooker et al., 1980; and Schjorring, 1991). A linear relationship of the amounts of NH3 absorbed by plants with the air NH3 concentrations was adopted in Manure-DNDC based on field observations (Hutchinson, 1972; Meyer, 1973; Cowling and Lockyer, 1981; Aneja et al., 1986; and Sommer and Jensen, 1991) (Equation 19 in Table A-1).

The NO3- existing in the soil profile can be leached by the infiltration water flow and hence leave from the manure life cycle.

**Table A-1. Equations of biogeochemical processes utilized in Manure-DNDC**

| Description | Equation |
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| 1. Feed N | FeedN = FeedR * FeedCP / 6.25 |
| 2. Urease activity | UREASE = k1 * DOC * WFPS * T,<br>where UREASE is urease activity (percent of urea hydrolized per day), DOC is dissolved organic carbon content (kg N/ha), WFPS is water-filled porosity, T is temperature (oC), and k1 is a coefficient (0.9 ha/kg/ oC)). |
| 3. Hydrolysis rate of urea | dUrea = [Urea] * UREASE,<br>where dUrea is daily hydrolyzed urea which is totally converted into NH4+, and [Urea] is concentration of urea (kg N/ha). |
| 4. Partitioning of fresh manure to MOM pools | if(manure_CN<rcnrvl)<br>{<br>Humads = ManureC;<br>VLL = 0.0;<br>LL=0.0;<br>RL=0.0;<br>} |

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| | else if(manure_CN>=rcnrvl&&manure_CN<rcnh)<br>{<br>Humads = (rcnrvl*rcnh*manure_CN - rcnh*ManureC)/(rcnh-rcnrvl);<br>VLL = ManureC - Humads;<br>LL=0.0;<br>RL=0.0;<br>}<br>else if(manure_CN>=rcnh&&manure_CN<rcnrl)<br>{<br>Humads = (rcnh*rcnrl*manure_CN - rcnh*ManureC)/(rcnrl-rcnh);<br>VLL = 0.0;<br>LL = ManureC - Humads;<br>RL=0.0;<br>}<br>else<br>{<br>RL = (rcnrr*rcnrl*manure_CN - rcnrr*ManureC)/(rcnrl-rcnrr);<br>LL = AddC - AddC3;<br>VLL = 0.0;<br>Humads = 0.0;<br>}<br>where ManureC- manure C content, manure_CN- manure C/N ratio, rcnrv- very labile litter C/N ratio, rcnrr- resistant litter C/N ratio, rcnh- humads C/N ratio, Humads- humads fraction, VLL- very labile litter fraction, LL-labile litter fraction, RL- resistant litter fraction |
| 5. Decomposition rate of manure organic carbon pool | dC/dt = CNR·μ·(S·kl + (1-S)·kr)·C,<br>where<br>C = decomposed manure organic C (kg C/kg manure per day),<br>t = time (day),<br>S = labile fraction of organic C compounds in the pool,<br>(1-S) = resistant fraction of organic C compounds,<br>kl = specific decomposition rate (SDR) of labile fraction (1/day),<br>kr = SDR of the resistant fraction (1/day),<br>μ = temperature and moisture reduction factor,<br>CNR = 0.2 + 7.2/(CP/NP) = C:N ratio reduction factor CP = C produced by potential residue decomposition per day (without CNR reduction factor) (kg C/ha),<br>NP = N produced by potential residue decomposition per day plus free NH4+ and NO3- in soil (kg N/ha).<br><br>C/N ratio=02.35, 20, 20, 8, 8, 8 and 8; SDR=0.074, 0.074, 0.02, 0.33, 0.04, 0.16 and 0.006 (1/day) for very labile litter, labile litter, resistant litter, labile microbes, resistant microbes, labile humads and resiatant humads, respectively. |

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| 6. NH4+/NH3 equilibrium | NH4+ = NH3 + H+;<br>Ka = [NH4+][OH-] / [NH3(l)],<br>[H+] = 10-pH;<br>H2O = H+ + OH-;<br>Kw = [H+][OH-],<br>Ka = (1.416 + 0.01357 * T) * 10-5;<br>Kw = 10^(0.08946 + 0.03605 * T) * 10-15<br>where Ka is equilibrium constatnt , Kw is water dissociation constant , [NH4+], [OH-] and [NH3(l)] are NH4+, OH- and NH3(l) concentrations (mol/l) in manure water, pH is manure pH, T is manure temperature. |
| 7. NH3 volatilization | FLUX(NH3) = [NH3(l)] * (T/T0)2 * (1-WFPS),<br>where FLUX(NH3) is NH3 flux, [NH3(l)] NH3 concentration in liquid phase, T soil temperature, T0 reference temperature (45oC), WFPS water-filled porosity. |
| 8. NH4+ adsorption by clay | FIXNH4 = [0.41 - 0.47·log(NH4)]·(CLAY/CLAYmax),<br>where<br>FIXNH4 = proportion of adsorbed NH4+,<br>NH4 = NH4+ concentration in the soil liquid (g N/kg),<br>CLAY = clay fraction in manure,<br>CLAYmax = maximum clay fraction (0.63). |
| 9. Nitrification | dNNO = NH4(t)·[1 - exp(-K35·Rt·dt)]·Rm;<br>where<br>dNNO = NH4+ converted to NO3- during time dt (kg N/ha/day),<br>NH4(t) = available NH4+ at time t (kg N/ha),<br>T = temperature (°C),<br>K35 = nitrification rate (25 mg/kg manure/day) at 35°C,<br>Rm = moisture reduction factor,<br>Rt = temperature reduction factors.<br>dt = time step (day) |
| 10a. Denitrifier growth rate: | (dB/dt)g = uDN·B(t),<br>where<br>(dB/dt)g = potential growth rate of denitrifier biomass (kg C/ha/day),<br>B(t) = total biomass of the denitrifier at time t (kg C/ha),<br>uDN = relative growth rate of the denitrifiers,<br>uDN = TE·(uNO3·PHNO3 + uNO2·PHNO2 + uN2O·PHNO3),<br>uNxOy = uNxOy,max·(C/(Kc,1/2+C))·(NxOy/(KNxOy,1/2+NxOy));<br><br>where<br>uNxOy = rel. growth rate of NO3-, NO2-, or N2O denitrifiers,<br>uNxOy,max = max. growth rate of NO3-, NO2-, or N2O denitrifiers,<br>C = concentration of soluble carbon in soil water (kg C/ha),<br>NxOy = concentration of NO3-, NO2-, or N2O in soil water (kg |

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| | N/ha),<br>Kc,1/2 = half-saturation value of soluble C in the Monod model (kg C/m3 soil water),<br>KNxOy,1/2 = half-saturation value of NO3-, NO2-, or N2O in the Monod model (kg N/m3 soil water).<br><br>TE = 2(T-22.5)/10, for T < 60,<br>TE = 0.0, for T >= 60<br>PHNO3 = 7.14·(PH - 3.8)/22.8<br>PHNO2 = 1.0<br>PHN20 = 7.22·(PH - 4.4)/18.8<br>T = soil temperature (°C).<br>PH = soil pH. |
| 10b. Denitrifier death rate | (dB/dt)d = Mc·Yc·B(t),<br>where<br>(dB/dt)d = death rate of denitrifier biomass (kg C/ha/hr),<br>Mc = maintenance coefficient of carbon (kg C/kg C/hr),<br>Yc = maximum growth yield on soluble carbon (kg C/kg C),<br>B(t) = denitrifier biomass at time t (kg C/ha). |
| 10c. Consumption of DOC by denitrifiers | dCcon/dt = (uDN/Yc + Mc)·B(t),<br>where<br>Ccon = consumed soluble C (kg C/ha),<br>uDN = relative denitrifier growth rate,<br>Yc = maximum growth yield on soluble carbon (kg C/kg C),<br>Mc = maintenance coefficient of carbon (kg C/kg C/hr). |
| 10d. Nitrate, nitrite and nitrous oxide consumption: | d(NxOy)/dt = (uNxOy/YNxOy + MNxOy·NxOy/N)·B(t)·PHNxOy·TE,<br>where<br>YNxOy = maximum growth yield on NO3-, NO2-,or N2O (kg C/kg N),<br>N = total nitrogen as NO3-, NO2-,and N2O (kg N/ha),<br>MNxOy = maintenance coefficient of NO3-, NO2-,or N2O (kg N/kg/hr),<br>B(t) = denitrifier biomass at time t (kg C/ha),<br>PH = soil pH factor,<br>TE = soil temperature factor. |
| 10e. The nitrogen assimilation rate by denitrifiers | (dN/dt)asm = (dB/dt)g·(1/CNRDN),<br>where<br>(dN/dt)asm = nitrogen assimilation rate by denitrifiers (kg N/ha/day),<br>CNRDN = C/N ratio in denitrifiers (3.45). |
| 10f. N2 and N2O emission from denitrification: | P(N2O) = 0.0006 + 0.013·PA;<br>P(N2) = 0.017 + 0.025·PA,<br>where<br>P(N2O) = emitted fraction of the total N2O evolved in a day, |

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| | P(N2) = emitted fraction of the total N2 evolved in a day,<br>PA = air-filled fraction of the total porosity, |
| 11a. Methane production | CH4p = (1.5* DOC + 0.9 * CO2 + 1.2 * Exud) * Ehf * Eftt * MAI * PHI;<br><br>MAI = T * EXP((T - 30) / 50) / 30 + 0.1, T<=30;<br>MAI = 30 * EXP((30 - T) / 50) / T + 0.1, T>30;<br><br>PHI = (7 / PH ^ 2 * EXP(PH - 7), PH<=7;<br>PHI=EXP(0.7 * (7 - PH)), PH>7;<br><br>Ehf= -0.0042 * (Eh/100) ^ 4 + 0.0706 * (Eh/100) ^ 3-1.557 * (Eh/100) ^ 2 - 2.3617 * (Eh/100) + 10.359;<br>Eftt=[(1 - EXP(-2 / NO3)) * 1.5] * (EXP(NH4 / 1000))<br>where CH4p is CH4 production rate (kg CH4-C/ha/day), Eh manure redox potential (mV), [DOC] concentration of DOC (kg C/ha), [CO2] concentration of CO2 (kg C/ha), MAI microbial activity index, T manure temperature (degree C), PH manure pH. |
| 11b. Methane oxidation | CH4o = .6 * [CH4] * (.1 + T / 30) ^ 2 / EXP(-(Eh + 150) / 150)<br>where CH4o is CH4 oxidation rate (kg CH4-C/ha/day), [CH4] is CH4 concentration (kg CH4-C/ha), and Eh is manure Eh (mv). |
| 11c. Methane diffusion rate | DIFF(L) = (CH4(L) - CH4(L + 1)) * T,<br>where DIFF(L) is CH4 flux (kg CH4-C/day) from manure, [CH4(L)] and [CH4(L+1)] are CH4 concentrations (kg CH4-C/ha) in and outside manure, respectively, T is temperature (degree C), PORO is air-filled porosity. |
| 12. Manure temperature in house | T(house) =T(air) - 0.001 * VR * (T(air) – 15)<br>where T(house) – house temperature (°C); T(air) – air temperature (°C); VR – ventilation rate (cubic meter/sec); |
| 13. Manure Eh | Eh = Eo + RT/nF * ln([O]/[W])<br>where<br>Eh is redox potential (volts), Eo is standard redox potential (volts), R is gas constant, T is temperature in kelvins, n is the number of transmitted electron, F is Faraday constant, [O] is concentration of oxidant (mol), and [W] is concentration of reductant (mol). |
| 14. Manure temperature in compost | dT(compost) = (H(gain) – H(loss)) / DM(compost) / HC(compost);<br>H(loss) = a * (Tc – Ta) * Ic,<br>where dT(compost) – daily change in compost temperature (°C); H(gain) – compost heat gain (MJ); H(loss) – compost heat loss (MJ); DM(compost) – compost mass (kg dry matter); HC(compost) – compost heat capacity (J/kg/K); Tc – compost temperature; Ta – air temperature; Ic – index of compost coverage; a – constant coefficient. |

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| 15. Slurry temperature in lagoon | T(d) = Ta * (1 – Fd) + Tb * Fd;<br>Tb = average(Ta1…Ta10),<br>Where T(d) is slurry temperature at depth d; Ta is coverage-adjusted air temperature; Tb is temperature at bottom of lagoon; Fd is depth index (0-1); Ta1 is air temperature of 1 day ago; Ta10 is air temperature of 10 days ago. |
| 16. CH4 ebullition from lagoon | CH4(eb) = b * T(l) * [CH4],<br>Where T(l) is lagoon slurry temperature, [CH4} is CH4 concentration in slurry, b is constant coefficient. |
| 17a. NH4+ and NH3 transfer from the bulk liquid to the interface liquid phase in lagoon | FLUX(NH3+NH4) = Kl * (([NH3](bl) + [NH4](bl)) – ([NH3](il) + [NH4](il)),<br>Where Kl-mass transfer coefficient in the liquid boundary layer; [NH3](bl)-NH3 concentration in the bulk liquid phase, [NH4](bl)-NH4+ concentration in the bulk liquid phase; NH3](il)-NH3 concentration in the interface liquid phase, [NH4](il)- NH4+ concentration in the interface liquid phase; |
| 17b. NH3 transfer from the interface liquid phase to the bulk air | FLUX(NH3) = Kg * ([NH3](ig) – [NH3](ag)),<br>where Kg – mass transfer coefficient in the air boundary layer; [NH3](ig)-NH3 concentration in the interface gas phase; [NH3](ag)-NH3 concentration in the air. |
| 17c. Equilibrium between NH3 in the interface liquid and NH3 in the interface gas phase | [NH3](ig) = Kh * [NH3](il),<br>where Kh – Hanry's coefficient, Kh(apparent)=Kh * F(uncorrected). |
| 17d. Equilibrium between NH3 in the interface liquid phase and total free N in the interface liquid phase | [NH3](il) = F(uncorrected) * ([NH3](il + (NH4](il)),<br>where F(uncorrected) – fraction of free NH3 in the interface liquid phase, which = 1/(1+(10^-pH/Ka),<br>pKa (acid-dissociation constant) = 0.0897 + 2729/T. |
| 18. CH4 production in anaerobic digester | potential_CH4_yield = DigesterCH4 * 0.672 * 12 / 16 * DigesterCapacity<br>if(doc> potential_CH4_yield)<br>day_digester_CH4 = day_potential_CH4_yield;<br>else<br>day_digester_CH4 = doc;<br>where potential_CH4_yield- daily potential CH4 yield (kg C/day), DigesterCH4- maximum CH4 yield (m3/m3/day), DigesterCapacity-digester capacity (m3), doc- DOC content in digester (kg C), day_digester_CH4- daily CH4 production (kg CH4-C/day) |
| 19. NH3 absorption by plants in field | PlantUp(NH3) = Vg * Air(NH3) * LAI * 0.864,<br>Vg = MaxVg * F(plant-N) * F(lsm);<br>F(plant-N) = Plant-N(act) / Plant-N(opt);<br>F(lsm) = LSM(act) / LSM(max)<br>Air(NH3) = Base(NH3) + Flux(NH3) * 10^9 / V(canopy) * LAI / (LAI + k2) * k3;<br>where PlantUp(NH3) is daily NH3 absorption by plant , Vg- NH3 deposition velocity (m/s); MaxVg is maximum velocity (0.050 m/s), |

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| | Plant-N(act) N content (kg N/ha) in crop, Plant-N(opt) optimum N content (kg N/ha) in crop, LSM(act) water content on leaf surface (cm), LSM(max) maximum water content on leaf surface (cm); Base(NH3) is atmospheric background NH3 concentration (ug/m3), Flux(NH3) daily NH3 flux (kg N/ha) from soil, V(canopy) volume of the room from ground to the top of canopy (m3), Height maximum height (m) of plant, LAI leaf area index, MaxLAI maximum LAI, and k2 and k3 are coefficients. |
| 20. Enteric CH4 production | EntericCH4 = GE * Ym / 55.65 * 12.0 / 16.0,<br>GE = FeedProtein * 17.0 * 0.6;<br>Ym = 0.171 (milk cow), 0.065 (beef or veal),<br>Where EntericCH4 is daily enteric CH4 production (kg C/day/milk cow); GE is gross energy demand by animal (MJ/head/day); FeedProtein is crude protein content in feed (kg protein/head/day); Ym is CH4 conversion rate (a fraction of gross energy); |
| 21. Enteric N2O production | Enteric_N2O = 0.001981 * dFeedN;<br>dFeedN = FeedN / 0.225333;<br>where Enteric_N2O is daily enteric N2O production (kg N/cow/day); dFeedN is daily feed N deficiency; and FeedN is daily feed N amount (kg N/cow/day). |

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# Appendix B: FTIR Background and Details

## Spectroscopy

Spectroscopy investigates the interaction between a defined source of electromagnetic radiation with a target sample. The way the emissive properties of the radiative source, usually some sort of light source, are perturbed depends upon the sample investigated. For example, molecules of gas can absorb electromagnetic radiation leading to molecular vibrations or rotations, with the frequencies that are absorbed by quantum theory being unique to each different type of molecule in the target sample. Therefore each molecule has its own characteristic absoprtion pattern over the electromagnetic spectrum.

Spectroscopic methods basically evaluate the concentration of the molecule investigated through Beer-Lambert's Law, which states that the fraction of light intensity transmitted through a gas is given by:

$$I/Io = \exp(-\sigma(\psi)NL) \qquad (1)$$

Where I and Io are the transmitted and incident powers respectively, L is the absorption path length (cms), and N would then be the concentration of the absorbing molecules in number of molecules per cubic centimeter. In this example $\sigma(\psi)$ is the wavenumber dependent absorption cross section in square centimeters per molecule.

## FTIR (Fourier Transform InfraRed Spectroscopy) Description

Fourier transform infrared spectroscopy began to come into its own in the early 1950s when experimental groups first built and tested high-resolution spectrometers. Today, commercial Fourier transform spectrometers are widely available. Aided by fast computers, which perform Fourier transforms quickly, FTIR spectrometers are used to make spectroscopic measurements in many diverse disciplines. This has led to FTIR technology being used in the development of many commercial instruments by companies such as IMACC, Nicolet, Midac, Bruker, Bomem, Unisearch Associates and ABB to name a few. Most of the commercial instruments employed in this type of infrared spectroscopy use an interferometer originally designed by Michelson to measure the speed of light as shown in Figure B-1.

The interferometer works by taking the entire incident beam of radiation from the source and dividing it into two paths with a beam splitter. The beam splitter is usually some non-absorbing film whose transmittance and reflectance are both approximately 50%. The beam splitter must also permit the transmission of the wavelengths (nominally 2-10 microns) employed for this type of spectroscopic measurement. Usually they are made of germanium. Therefore the source radiation incident on the beamsplitter is divided into two parts. One of the paths goes to a fixed mirror while the other path goes to a moving (translating) mirror. When the position of the translating mirror is continuously varied along an axis collinear to the source, an interference pattern I(x) is generated as the two phase shifted beams interfere with each other. By smoothly translating one mirror, the optical path difference (OPD) is x=2L (where x is

twice the distance L traveled by the translating mirror). This optical path difference (also called retardation,) between the beams traveling to the fixed and the moving mirrors will be the same for all wavelengths of light. This leads to two boundary conditions. First, when the two beams have traveled the same distance, they will be in phase and thus when they recombine at the beam splitter, will interfere constructively. Second, when the movable mirror is at a distance twice that of the fixed mirror, the two beams will be out of phase with each other and interfere destructively. By moving the translating mirror at a constant velocity, the signal at the detector will vary sinusoidally. The time varying component is the only component that is important in spectroscopic measurements and is called the interferogram. The actual signal measured at the detector will depend on the beamsplitter, detector response at different wavelengths and the emission light source.

The specific intensity Ik(x) can be derived for the source energy at a single wave number k by

$$I_k(x) = J(k)\,\langle T(k)\rangle\,\tfrac{1}{2}[1 + \cos(kx)] \qquad (2)$$

where J(k) is the incident intensity and <T(k)> is the averaged beam splitter transmission function. Since cos(kx) is an even function, the interferogram will be symmetrical about the white light fringe. Since the resolution of a fourier transform spectrometer increases with increasing optical path difference, the maximum spectral resolution is achieved by using the entire available translation distance to measure only one side of the interferogram. Figure B-2 provides a typical interferogram.

However, in order to maximize the signal-to-noise ratio (by avoiding the slight overhead incurred in switching the direction of stage motion), both sides of the interferogram can be measured, yielding a so-called "two-sided" interferogram. Two-sided interferograms contain two measurements of each interferogram point per scan, but can only achieve half the optical path difference (and therefore half the spectral resolution) of one-sided scans. Because one-sided interferograms transform to real spectra, no explicit information on the interferogram phase is available, although phase problems do show up as anomalous spectral baselines.

Two-sided interferograms transform to complex spectra (they have two pieces of information per frequency), allowing phase errors to be directly measured as a function of frequency. Two-sided scans are therefore extremely useful for examining alignment of the optics and other potential instrumental problems. As already mentioned, a perfectly aligned instrument with no phase errors will produce completely symmetric interferograms whose transform will have zero imaginary part over all frequencies in the passband. The total intensity measured for a given OPD x from radiation at all wave numbers is found by integrating which is equivalent to applying the inverse Fourier cosine transform Fc-1

$$
\begin{aligned}
I(x) &\equiv \int_0^\infty I_k(x)\,dk = \frac{1}{2}\int_0^\infty [1+\cos(kx)]\,(T(k))\,J(k)\,dk \\
&= \frac{1}{2}\int_0^\infty (T(k))\,J(k)\,dk + \frac{1}{2}\int_0^\infty \cos(kx)\,(T(k))\,J(k)\,dk \\
&= \tfrac{1}{2}I(0) + \frac{1}{2}\int_0^\infty \cos(kx)\,(T(k))\,J(k)\,dk \\
&= \tfrac{1}{2}I(0) + \tfrac{1}{2}\mathcal{F}_x^{-1}[(T(k))\,J(k)].
\end{aligned}
\tag{3}
$$

The FT-IR spectrometer generates the infrared spectrum of a given sample by calculating the ratio of the signal obtained by scanning air (empty beam) to the signal obtained by scanning the sample gas.

This process is schematically illustrated in figures B3-4, for the FTIR analysis of styrene, (taken from the Columbia University web site (www.columbia.edu/ccnmtl/draft/dbeeb/chem-udl/spectrometer.html)). First an interferogram of the source (background) is scanned (figure B-3 left), and then transformed into a single beam spectrum (figure B-3 right) and stored in computer memory. The sample, (in this case containing styrene), is then sampled by many possible ways, either extractively to a sample cell, in-situ or open-air and the interferogram of the sample gas is scanned (figure B-4 left), and then transformed into a single beam spectrum and stored in computer memory.

The ratio between the two single-beam spectra, in computer memory, is calculated and the "double beam" presentation with a flattened baseline is produced. The features present in the background spectrum correspond to the emission profile of the source, the optical efficiency, or detectivity of the detector, the absorption of atmospheric water, and gaseous CO2. The ratio process compensates for these effects and they don't appear in the spectrum of the sample as shown in figure B-5.

By comparing the resulting IR spectrum of styrene to stored calibration spectra of styrene the concentration of styrene in this sample can be ascertained. It is important to note that calibration spectra are temperature and pressure dependent and accurate IR measurements require stored calibration spectra at the temperature and pressure of the sample gas.

## CE-CERT/UCR FTIR

Figure B-6 is a picture showing the CE-CERT/UCR FTIR purchased from IMACC in April 2001. This FTIR has been used primarily for the measurement of on road exhaust gases in determining emissions from ULEV (ultra low emitting vehicles) and is now available for this project.

We have also subcontracted IMACC to provide us with an additional FTIR system to conduct open path FTIR measurements in as follow-on to this project. The specifications for the CE-CERT/UCR FTIR are found on table B-1.

The CE-CERT FTIR can display data or spectra during real time acquisition or after the fact. The FTIR is configured to open and automatically run a specified script when it is started. The monitor allows for custom windows to be created so that we can graphically display spectra or interferograms, as well as plotted data and tabular lists of diagnostics or gas concentrations. The layout for the monitor is also saved so multiple display layouts can be set up and simply opened to configure the screen for a particular application.

A typical FTIR display is shown in Figure B-7. Here the top most window has buttons for loading, starting, and stopping the script. The next window has two panes. The one on the left displays gas concentration data along with the analysis (2 ◎) errors.

The window on the right has selected diagnostic parameters displayed. In this case these are the current system status, the percent complete for the current averaging interval, the number of scans complete, the number of "batches" or averaging intervals of data produced, the number of good scans in the last averaging interval, the number of bad scans in this interval (if any), the averaged pressure and temperature for the last completed measurement interval, and the peak interferograms voltages.

The lower window was set up as a tab window with two tabs. One tab brings up plots of the gas concentrations and the tab selected here shows spectra.

In this case the single beam and absorbance spectra are displayed. In all windows, a right mouse click brings up configuration menus that allow the user to select the type of plot/tabulation displayed and the parameters or data to be shown. Once the monitor is set up as desired and linked to a script, all that is required to start data acquisition, processing, and display is to start the monitor.

## Experimental Preparation and Method Development

### FTIR Preparation

An IMACC FTIR was readied for use in ambient measurements of N2O. The FTIR is based on a Nicolet intereferometer, the unit has been encased in a Nema 4 enclosure and structurally designed for field use by the manufacturer IMACC. The FTIR was removed from its previous sampling system. A sampling pump, sampling lines, and purge lines were installed. The FTIR was moved and set up in the Atmospheric Processes Laboratory. Operating parameters for the IMACC FTIR appropriate for identification of N2O in non-dried ambient samples were chosen and set up. The parameters for the interferometer and gas cell are listed in tables B-2 and B-3.

A quantification method file and standard spectra files appropriate for identification and quantification of N2O in ambient samples were configured in the methods system. The species selected are listed in Table B-4 as are the standards of the stored spectrum in the method. For example the stored spectrum for CO was done with a calibration gas of 10.5 ppmV at 25 C at a

path of 8.3 meters (our test cells pathlength). These stored spectra, at known pressures, temperatures and concentrations, are used to determine the concentrations of the measured spectra when a classical least square fit is applied to the measured spectra with the stored calibration spectra. The wavelengths of analysis for the species measured are listed below in Table B-5, these represent the frequencies of interest for the entire method, which incorporates the 7 subject species. Table B-6 lists the subject species and whether the other gases measured and included in the method development are an interferent to the subject species.

Spectra of dry zero nitrogen were collected for use as background spectra. Spectra of nitrogen, ambient air, and an N2O gas standard (100 ppmV N2O, balance N2) were collected in order to evaluate noise levels and response to N2O.

Figure B-8 shows the single beam power spectrum for zero nitrogen. The small power absorption that occurs near 2350 cm-1 is due to residual CO2 in the sample path. The numerous lines centered around 1500 cm-1 are due to residual water in the sample path. This single beam spectrum is used as a background spectrum. The transmittance spectrum for a sample is calculated by dividing the single beam spectrum of a sample by the single beam spectrum of the background.

Figure B-9 shows a transmittance spectrum for ambient air. In regions of the spectrum where the sample absorbs little power, the transmittance is near 100%. In regions near 2350 cm-1 and 1500 cm-1 nearly all of the power is absorbed by CO2 gas and H2O gas respectively, and the tranmisttance is nearly zero.

Absorbance is calculated as the negative logarithm of transmittance

$$abs = -\log(I_{sample}/I_{background}) \qquad (4)$$

where Isample and Ibackground are the single beam spectra of the sample and background respectively. Figure B-10 shows the absorbance spectrum of the ambient sample.

Figure B-11 shows the absorbance spectrum of 100 ppmV N2O in nitrogen, using our cylinder calibrated gas standard. When this method is applied to laboratory indoor ambient air, the method reports concentrations ranging from 0.250 to 0.320 ppm, with uncertainty on the order of +/- 0.030 ppmV.

## Sampling System Preparation

The sampling configuration was designed and has been constructed to have 7 inputs and 1 outlet. Figure B-12 shows the sampling layout for the instrument configuration. All valves are Teflon with 3/8 inch orifices. The inlets are for the following:

- 1–meter elevation on tower
- 2-meter elevation on tower
- 5-meter elevation on tower
- 10-meter elevation on tower

- Trailer Interior
- Spare
- spare

The single outlet is to the FTIR.

We set longer integration times at each elevation, basically three minutes, so that we can give a complete measurement cycle once every 15 minutes which includes cell purge times. The longer integration times will improve the sensitivity for the N2O measurement.

Also that all lines from the FTIR sampling system to the individual measuring points were made to be the same length and same volume to reduce anomalies or artifacts from sampling. Also note that the sampling system has been made automatic with computer control. The valve system was programmed using a Campbell data logger, which recorded the sequence of sampling and set each sampling interval at each height for a period of three minutes. This allowed time to completely purge the sampling cell of the previous sample. This system was designed and operated to collect the following:

- H2O Concentration
- CO2 Concentration
- CO Concentration
- N2O Concentration
- CH4 Concentration
- NH3 Concentration
- Hydrocarbon Concentration

## Field Measurements and Results

### Sampling Site

The FTIR was set up on the campus dairy at California State University Fresno (CSUF) at the south end of the dairy dry lot. The dairy is located north and west of the intersection of E Barstow Ave and North Chestnut Ave in Fresno. Figure B-13 is an aerial image of the dairy, and the red block is the general location of the sampling site. The actual sample collection point is north of the red block visible in the figure, and is located about two meters south of the fence bordering the southernmost lot. The sampling points were on a ten-meter tower to collect gas samples and meteorological data from various elevations. CSUF provided the site, a trailer, and the tower.

CE-CERT collected gas samples at heights of one, two, five, and ten meters. CSUF collected wind speed and wind direction at heights of one, two, and ten meters, and collected temperature and relative humidity at a height of two meters. The support trailer was located as far south of the tower as possible to minimize its effect on northerly winds. Distance from the trailer to the tower was a few meters. Figures B14-B17 illustrate the equipment setup and general characteristics of the dairy.

## Sample Transport and Sequencing

Inside the trailer, CE-CERT set up a Fourier Transform Infra-Red (FTIR) Spectrometer to measure N20. The FTIR sampled through a bank of five valves that switched sequentially through a sequence of five sample valves. Each of the four sample lines leading to the collection points on the tower were the same length: 100 feet. The fifth line was very short and sampled from inside the trailer. This fifth sample line is available for testing bag samples or cal gases without disrupting normal sampling. The lines to the elevated sampling points on the tower were sampled in this order: 1 m, 2 m, 5 m, 10 m, indoor. The sample flow switched from one elevation to the next every three minutes. A complete sampling cycle took 15 minutes. Sample flow rate was nominally 7 liter per minute (lpm), so that transit time though the 100 foot sample line was about 9 seconds. The air sampling information is summarized in Table B-7.

## Field Setup of FTIR

The FTIR was set up to measure sub-ppm levels of nitrous oxide (N2O) with a resolution of roughly 10 ppb. Details of the FTIR operating parameters are shown in table B-8.

These parameters also allow measurement of CH4, NH3, CO, and CO2 at the same time. The calibration method used to quantify the spectra is based on spectral measurements made at temperatures and pressures slightly different than the temperature and pressure used to collect samples in this study.

Factors to correct for temperature and pressure were developed with the assistance of the instrument manufacturer and incorporated in the final data set.

The FTIR measures light absorption in a continuously flowing gas cell having a path length of 8.28 meters and a cell volume of 2.0 liters. Twenty spectral scans are collected and averaged for each sample, which leads to a sample collection time of slightly less than 30 seconds.

The valve system collects at each sample height for 3 minutes, therefore six samples will be measured by FTIR at each height. The first point and the sixth point at each height are discarded because the sample switching period and the FTIR sampling periods are not exactly synchronized, and therefore the first or sixth points can include a sample line transition. Points two and three are discarded to allow sample transit time and cell flushing time. Points four and five are retained as samples.

Figure B-18 shows the inside of the CSUF trailer where the FTIR was installed. Note that the computer controlled sampling system was located in the trailer as well.

## Example Results

Preliminary results are shown on Figures B19-B21. Figure B-19 shows an example of CO2 data and sample line marker. The blue points are CO2, the pink points are valve position marker. The points were collected every 30 seconds, the valves switched every three minutes. Valve 0 controls the sample line inside the trailer. This valve has a more restrictive orifice than the other

valves, which causes the pressure in the sample cell to be much lower than when sampling the tower lines. The reduced cell pressure during valve 0 sampling means that the mass of CO2 in the cell for a given ppm is lower than the mass of CO2 for the same ppm in the cell at normal pressure. Thus, the FTIR signal is lower.

This is useful to keep for the entire data set as we could flag when the data was measured in the trailer and time synchronize the valve switching measurements with the FTIR as the FTIR was not exactly 30 seconds but was approximately 29.7 seconds. This alleviated any mix up in combining the data sets.

Because the data have not yet been corrected for pressure and temperature, the reduced signal is apparent in the figure. The yellow points in the figure are the fifth data point collected during each three minute sample collection period.

The figure demonstrates the correct alignment of FTIR sample selection with valve position.

Figure B-20 shows the same type of plot except for N2O. The N2O shows the same reduction in signal as the CO2 for the same reason during valve 0. Both figures show very little variation in CO2 or N2O concentration among the other sampling heights. Figure B-21 show the N2O data over the next couple of hours. The N2O sampled at one meter and two meters is measurably higher than the N2O measured at five meters and ten meters.

In particular examine the sample periods beginning at 18:45, 19:30, and 19:45. This is representative of a gradient from an area source, although we are only measuring over a small area, with an open path FTIR we would be able to make measurements over the whole area source monitored.

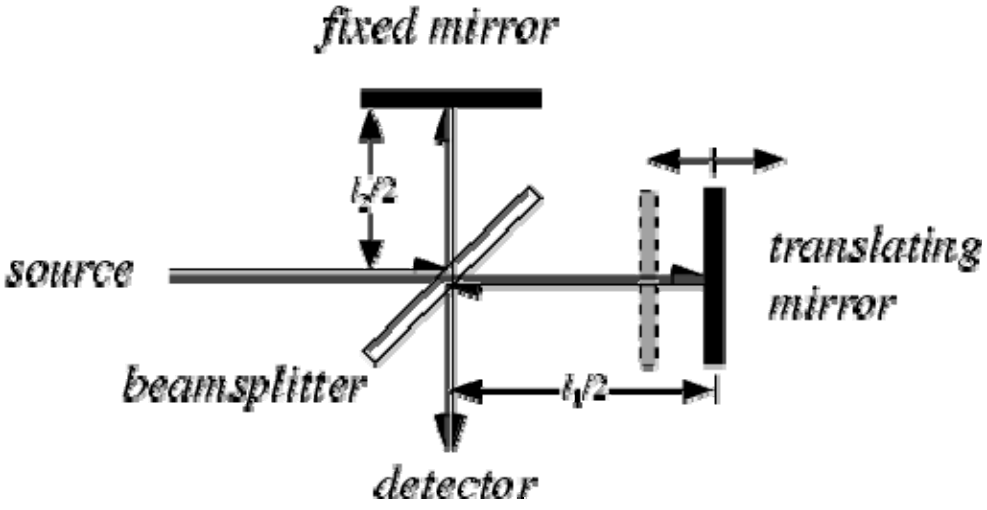
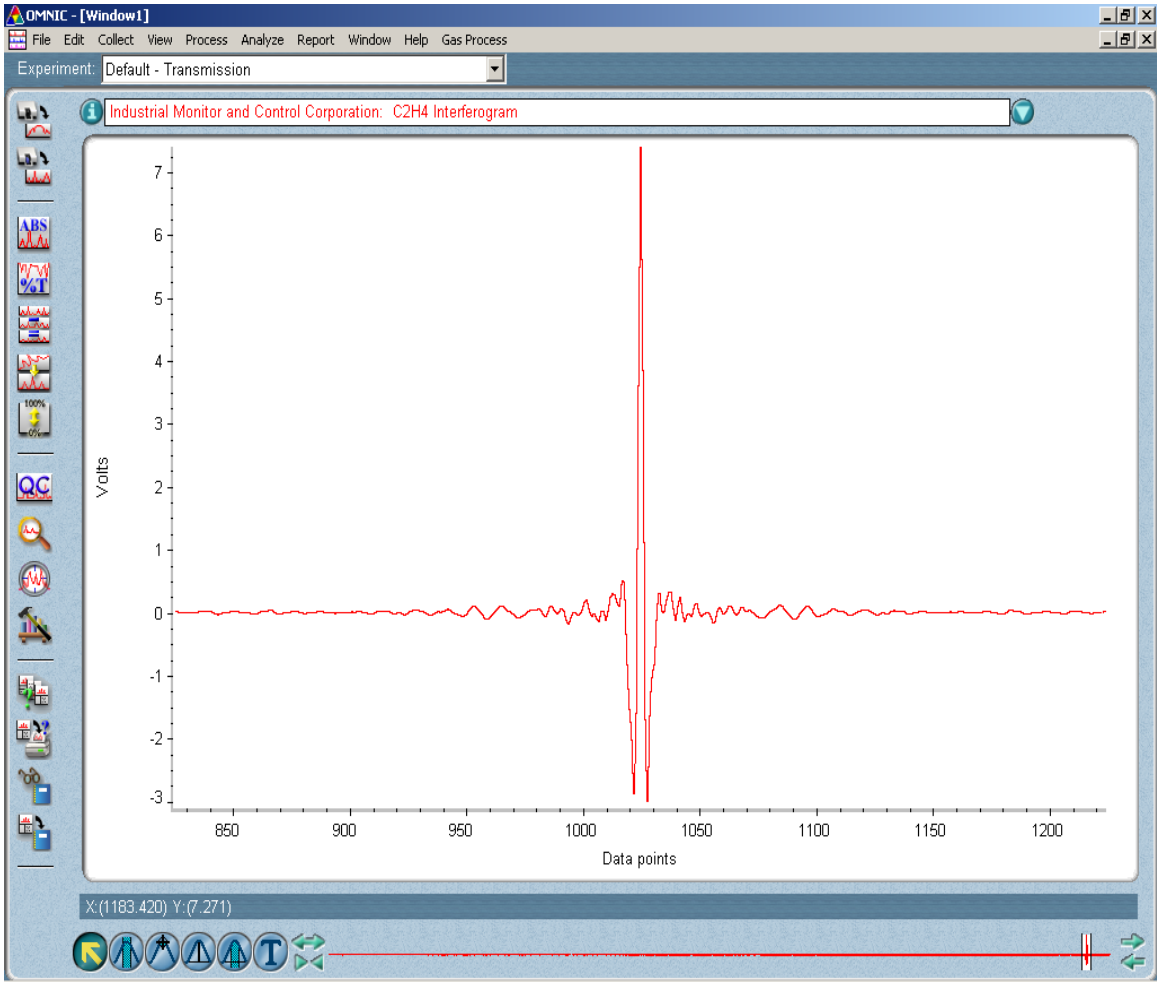



**Figure B-1: Typical Michelson Interferometer.**




.

**Figure B-2: Typical Interferogram, In This Example Ambient Air Containing High Level of C2H4**

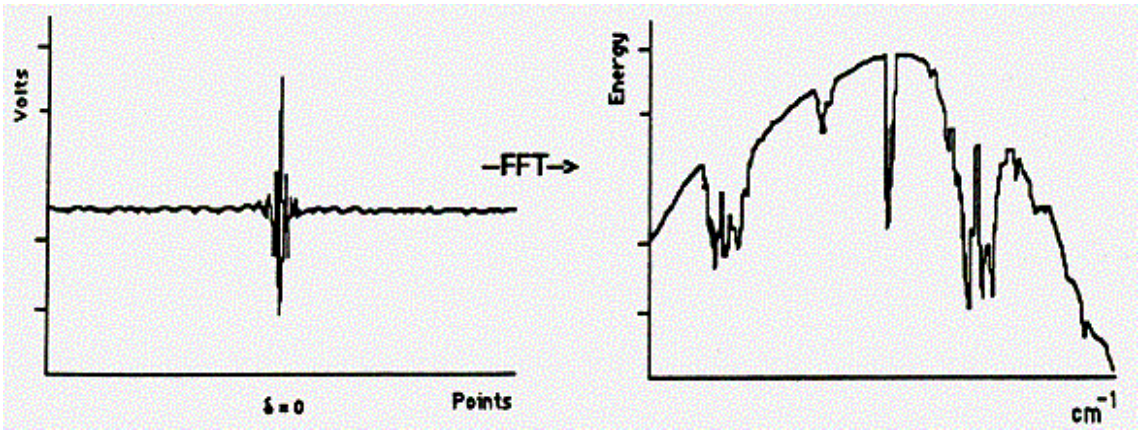



**Figure B-3: Interferogram Of The Source Background (Left), And Resulting Transformed Single Beam Spectrum (Right)**

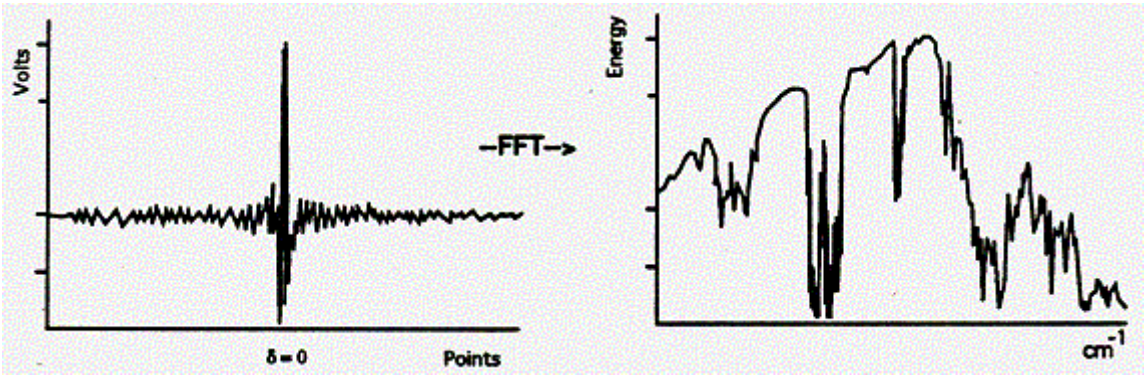



**Figure B-4: Interferogram Of The Gas Sample Containing Styrene (Left), And Resulting Transformed Single Beam Spectrum (Right)**

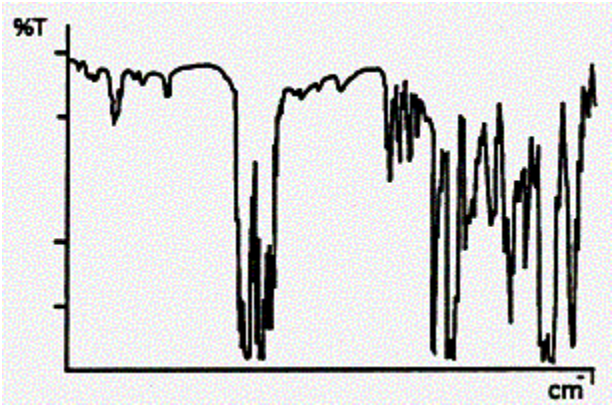



**Figure B-5: Resulting IR Spectrum of Styrene**

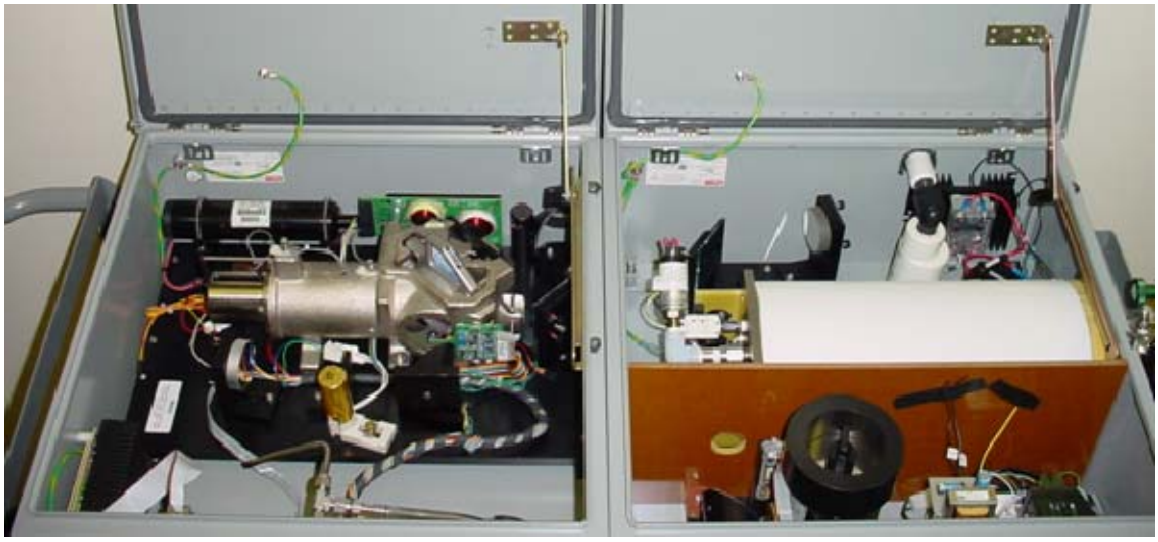


**Figure B-6: The CE-CERT/UCR FTIR (left) purchased from IMACC and the 8.3 meter cell (right)**


**Figure B-7: A typical FTIR display from the UCR/CE-CERT FTIR**

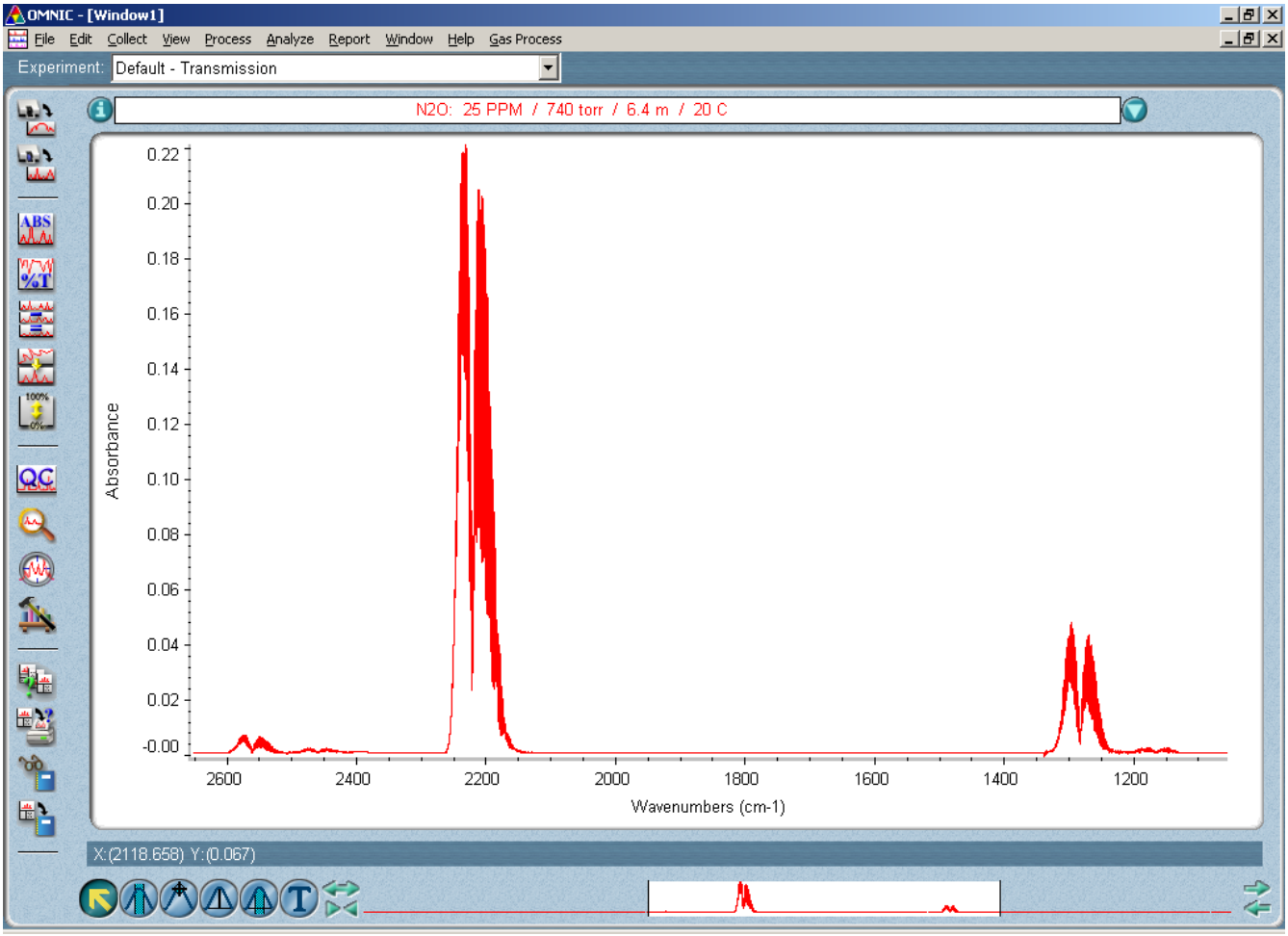



**Figure B-8: Plot of N2O Spectra using 25 ppmV certified calibration gas into a 8.3-meter White Cell that was controlled at 10 C and 740 torr.**

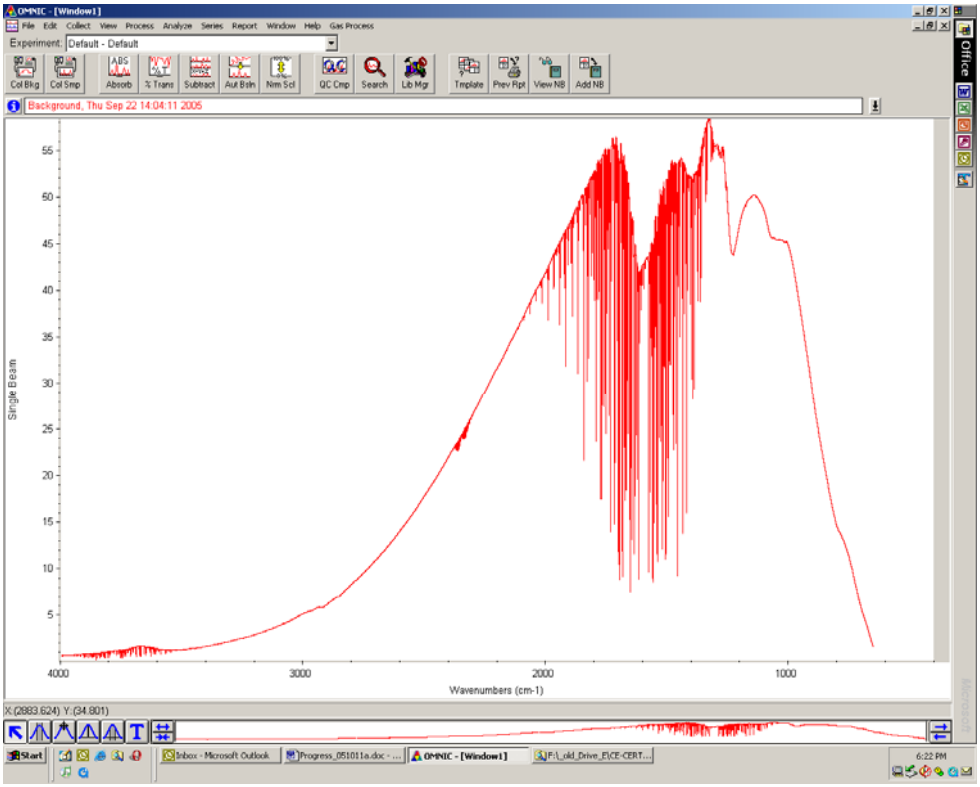



**Figure B-9: Single Beam Spectrum of Nitrogen**

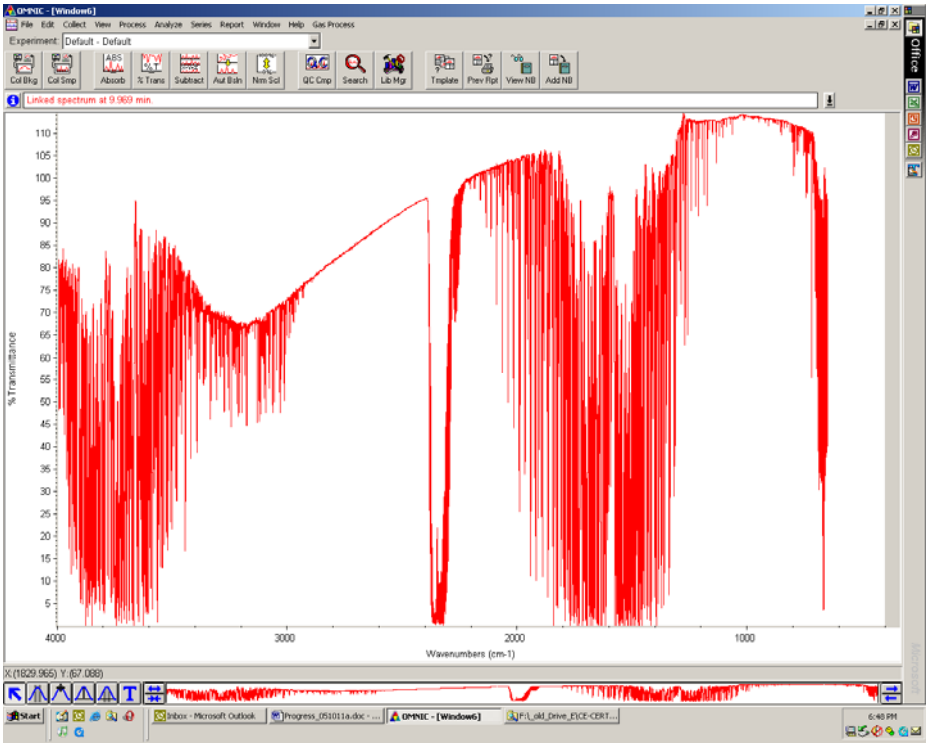



**Figure B-10: Transmitance Spectrum of Ambient Air**

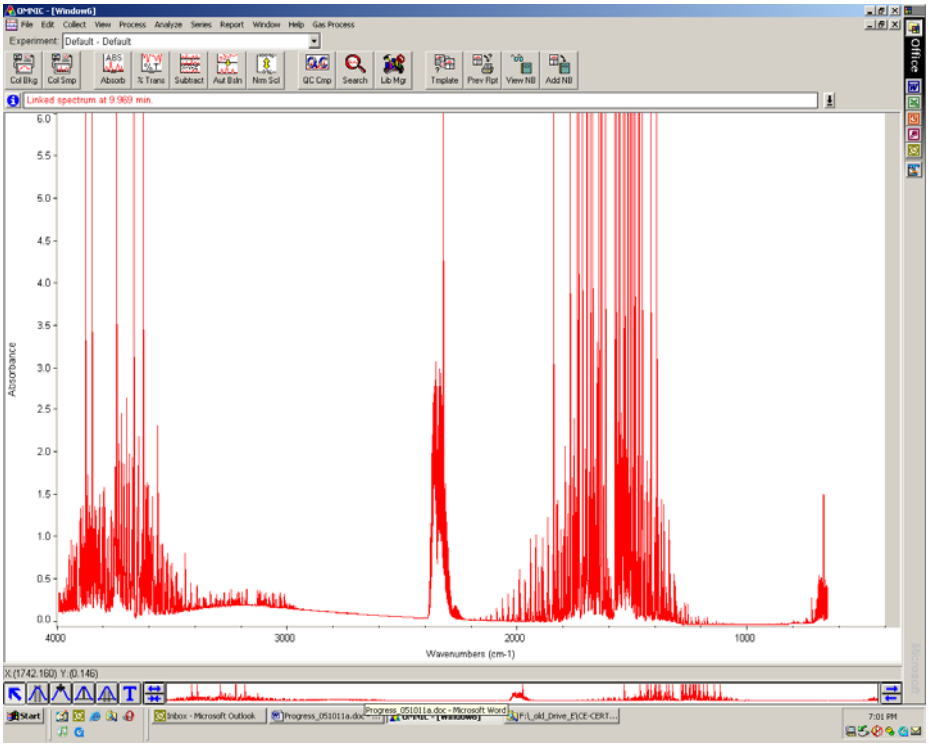



**Figure B-11: Absorbance Spectrum of Ambient Air**

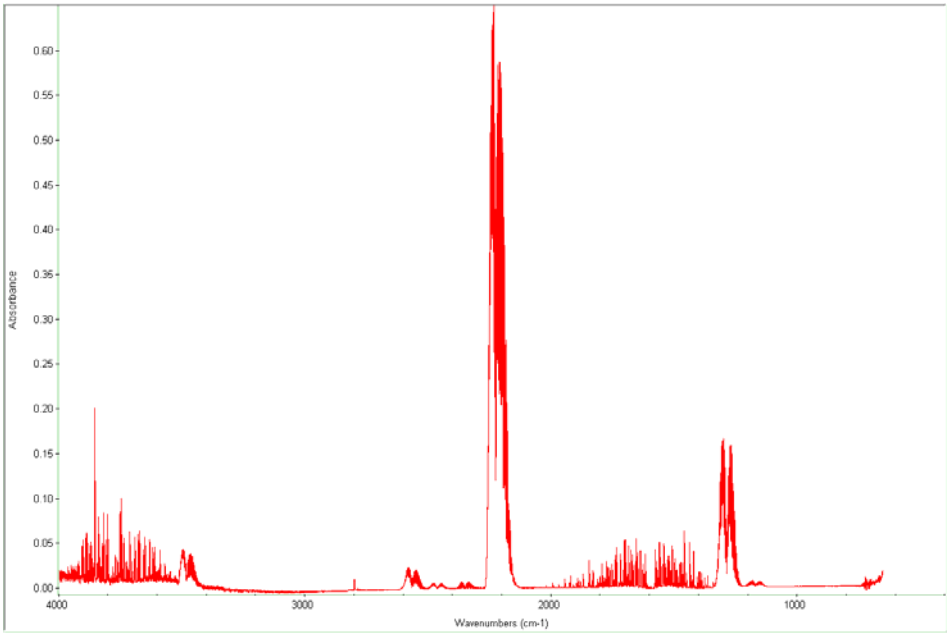



**Figure B-12: Absorbance Spectrum of Nitrous Oxide (100 ppm) in Nitrogen**

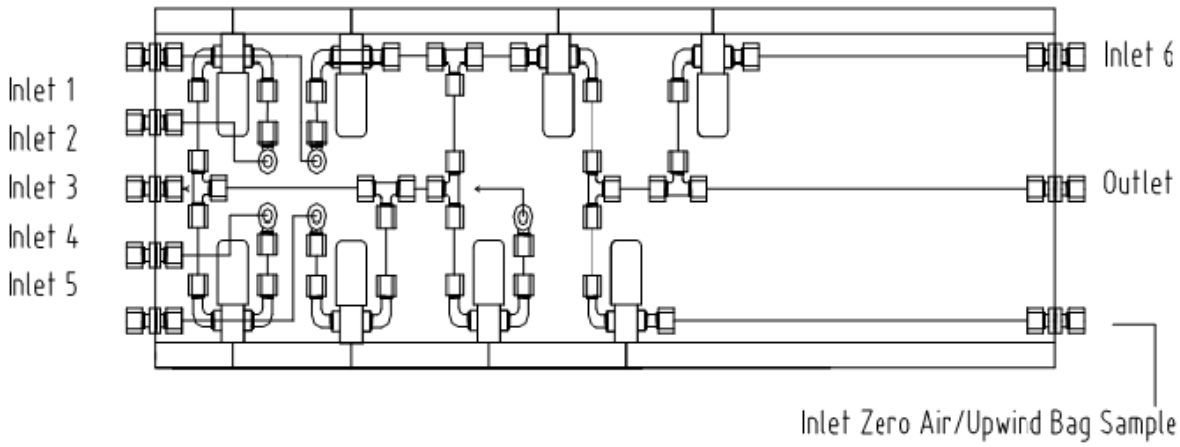



**Figure B-13: Physical layout of the Constructed Sampling System for the N2O**


**Figure B-14: Aerial view of dairy and sampling site location**

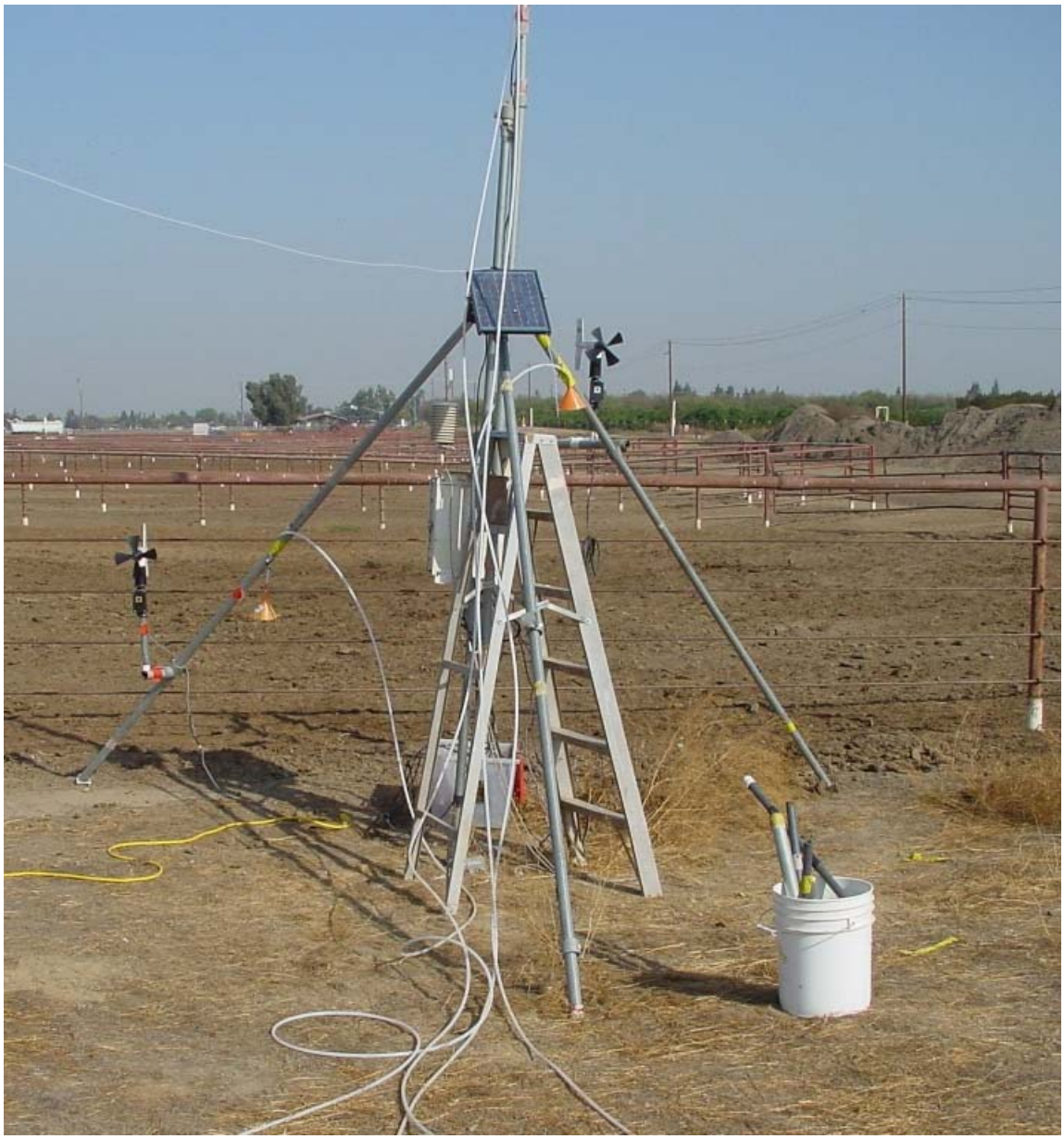
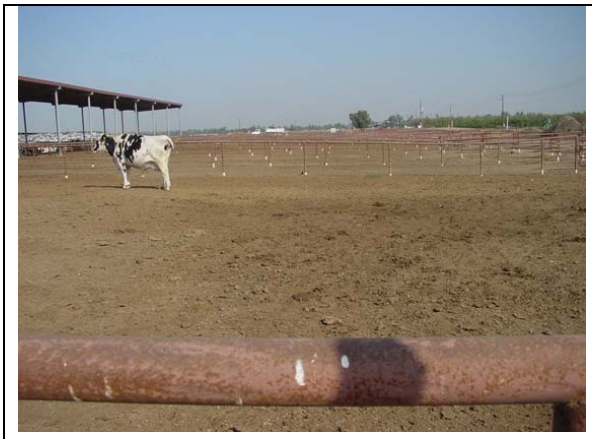


**Figure B-15: Sample collection tower. It shows wind sensors at one and two meters, the temperature/RH sensor at two meters, and gas sampling points at one and two meters. The figure also shows the proximity to the dry lot.**

**Figure B-16: View of site, photo taken from the southeast. It shows the relationship of the tower to the trailer, and the five meter gas sampling point can also be seen.**

**Figure B-17: Dry lot surface (and nearby cows) indicating the proximity of cows to the sampling points from time to time.**



View from tower to North

View from tower to East

View from tower to South

View from tower to West

**Figure B-18: Views from tower to points of compass, looking due north, east, south, and west.**

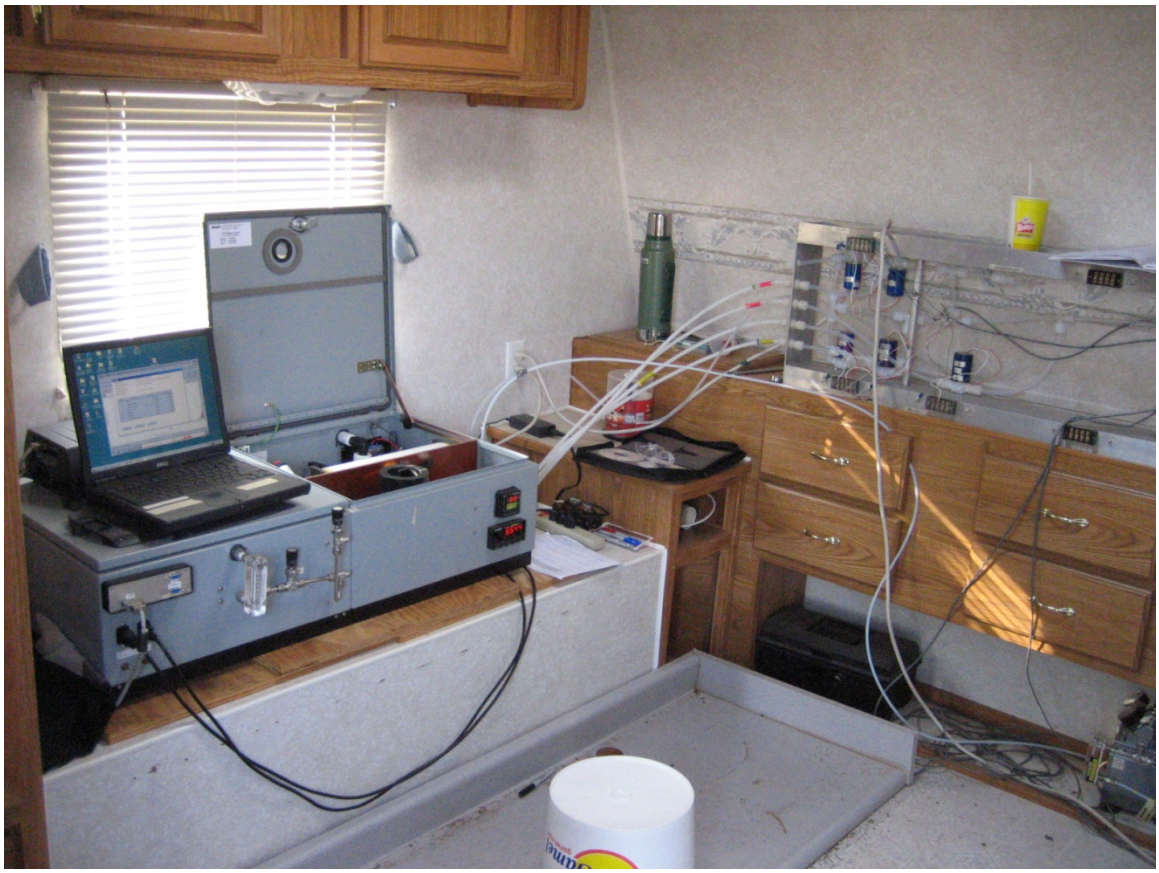


**Figure B-19: IMACC FTIR Instrument in Instrumentation Trailer (left) with UCR Built Sampling System (right)**

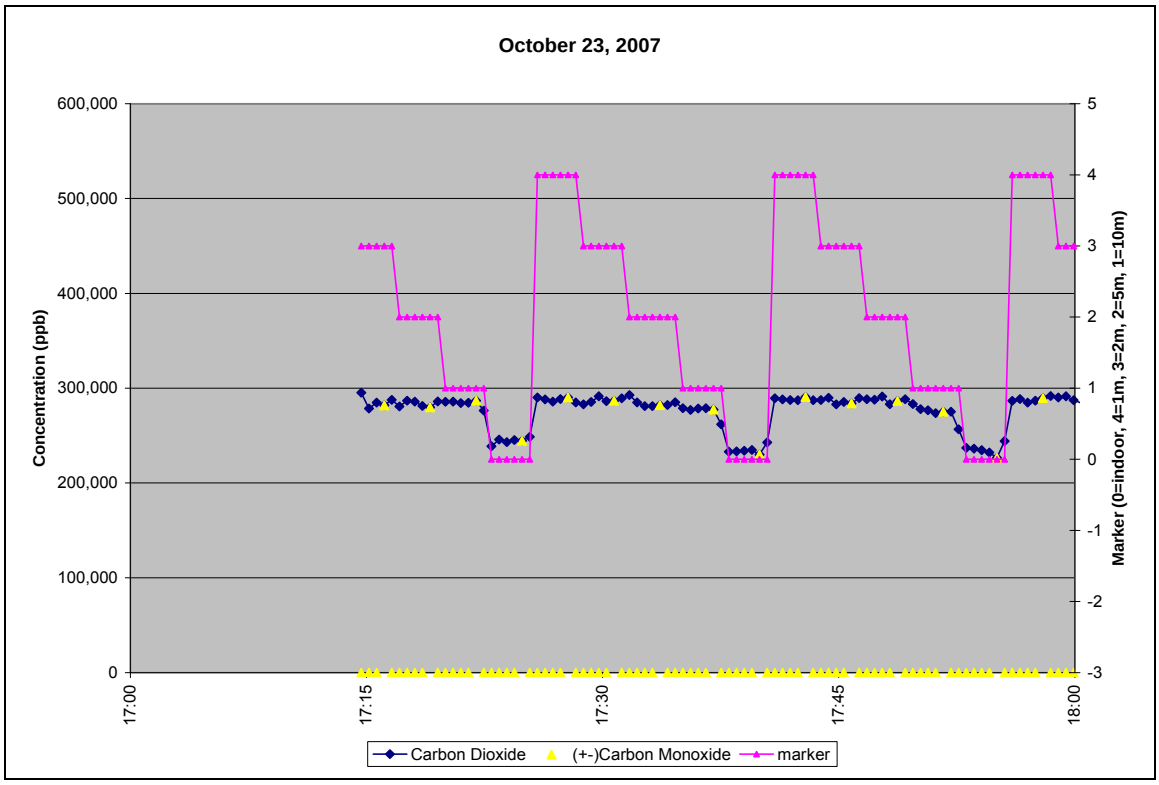



**Figure B-20: Example of sequential CO2 data and valve marker**

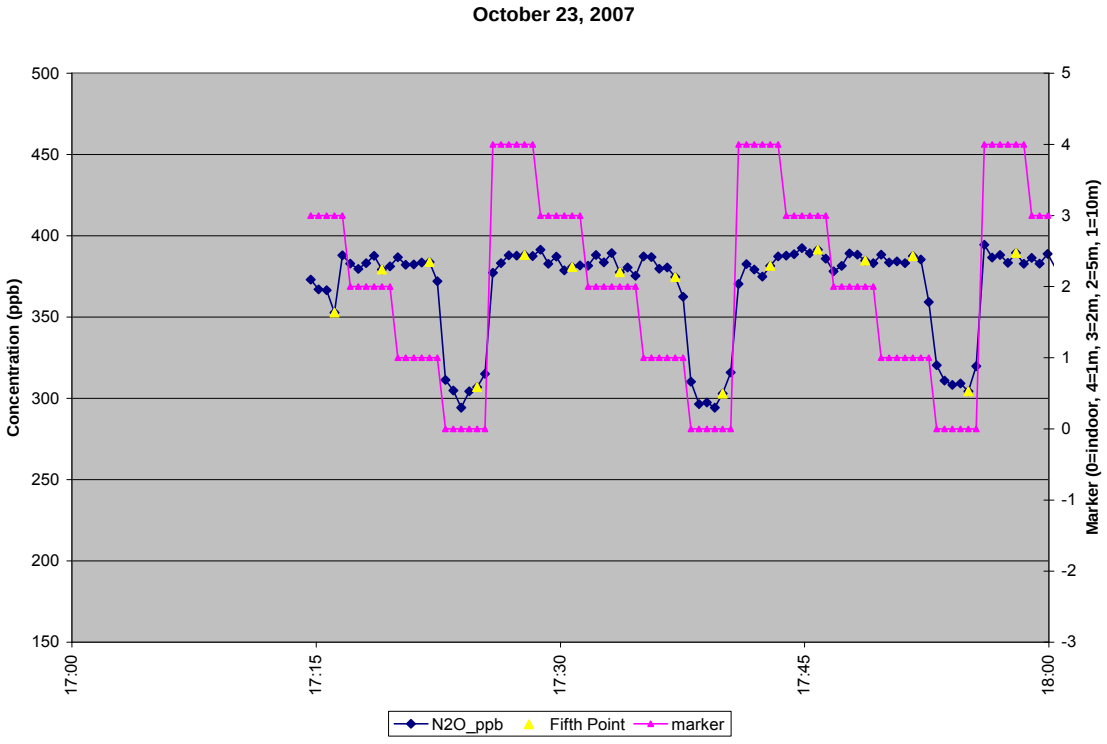



**Figure B-21: Example of sequential N2O data and valve marker**

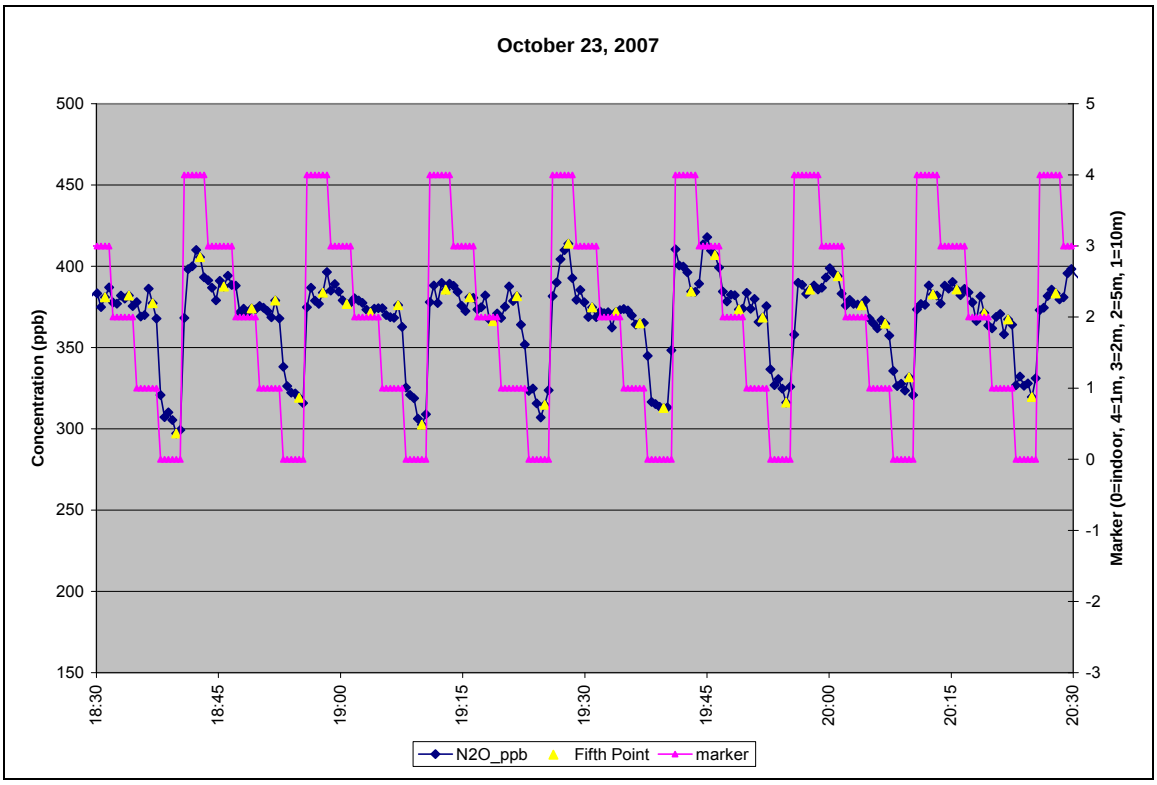



**Figure B-22: Example N2O data showing variation with sample height**

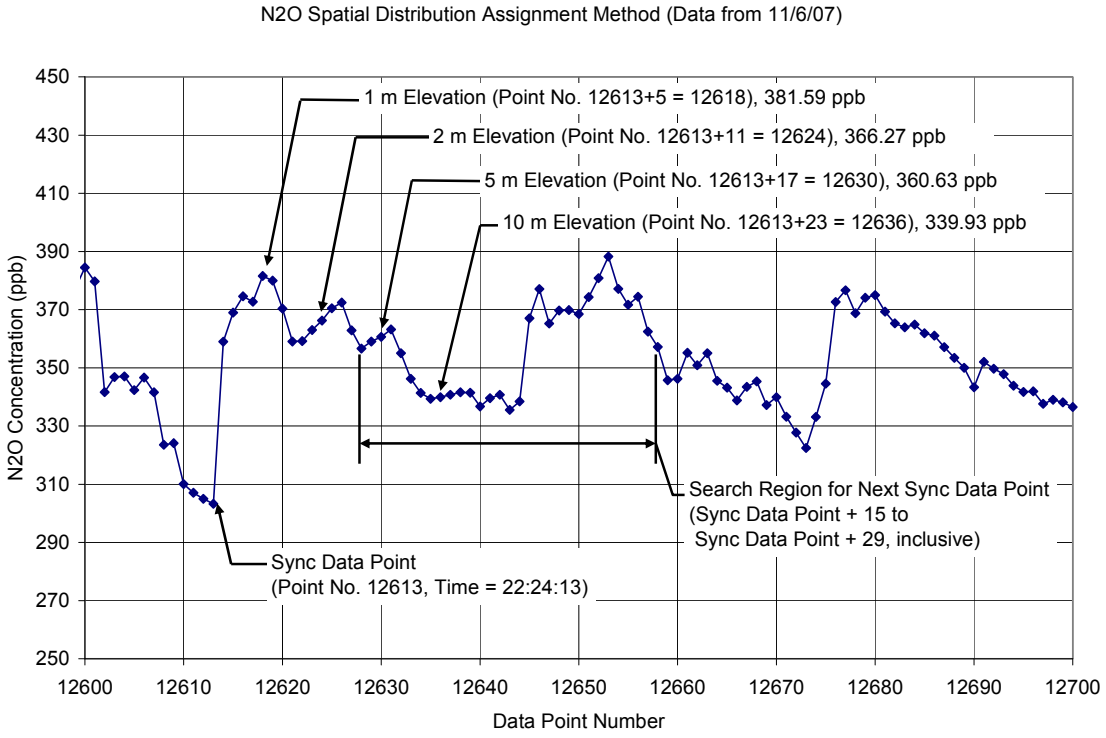



**Figure B-23: Illustration of Method to Assign N2O Measurements to Each Measurement Location**

**Table B-1: UCR/CE-CERT FTIR Specifications**

| | |
|---|---|
| Supplier: | IMACC FTIR |
| Model: | B-ZME20-C |
| S/N: | B001001D |
| Date purchased: | April, 2001 |
| Resolution: | 0.5 cm-1 |
| Wavenumber: | 650 to 4000 cm-1 (400 to 4000 cm-1) |
| Max Scan Rate: | one scan per 1.4 seconds |
| **Cell Accessory** | |
| Model: | E-1000-C |
| S/N: | E001201D |
| Date purchased: | April 2001 |
| Volume: | approx 2.0 liters |
| Path: | 8.28 meter |
| Software:Nicolet | OMNIC E.S.P. 5.2a |

Quantification Method: Classical Least Squares (CLS)

**Table B-2: Interferometer parameters**

**Interfereometer:**

| | |
|---|---|
| Resolution: | 0.5 cm-1 |
| Mirror Velocity: | 1.899 cm/sec |
| Aperture: | 10 |
| Gain: | 1.0 |
| Zero filling: | None |
| Apodization: | Happ-Genzel |
| Sample Spacing: | 2 (yields spacing of 0.241 cm-1) |
| Spectral Range: | 650 to 4000 cm-1 |

**TableB-3: Gas Cell parameters**

**Gas Cell:**

| | |
|---|---|
| Temperature: | 30 oC |
| Pressure: | 720 torr |
| Optical Pathlength: | 8.3 meters |

**Table B-4: Standards Information**

| Component Abbr. | Code | File Name | Conc. (ppm) | Temp. (C) | Press. (Torr) | Path. (m) |
|---|---|---|---|---|---|---|
| H2O | H2O | c:\omnic\spectra\ref5\h2oc1s.spa | 1.0 | 23.0 | 750.0 | 8.3 |
| CO2 | CO2 | c:\omnic\spectra\ref5\co2-400.spa | 400.0 | 25.0 | 760.0 | 8.3 |
| CO | CO | c:\omnic\spectra\ref5\ref5002b.spa | 10.5 | 25.0 | 735.0 | 8.3 |
| N2O | N2O | c:\omnic\spectra\ref5\ref5006.spa | 25.0 | 20.0 | 740.0 | 8.3 |
| CH4 | CH4 | c:\omnic\spectra\ref5\ref5009.spa | 175.0 | 20.0 | 740.0 | 8.3 |
| NH3 | NH3 | c:\omnic\spectra\ref5\ref5007.spa | 543.0 | 20.0 | 740.0 | 8.3 |
| HCONT | HCONT | c:\omnic\spectra\ref5\hcont.spa | 30.0 | 25.0 | 650.0 | 8.3 |

**Table B-5: Analysis Frequency ranges (note all regions are in wavenumbers)**

| Regions | | | Windows | | |
|---|---|---|---|---|---|
| # | Start | End | # | Start | End |
| 1 | 723.30 | 767.00 | 1 | 723.30 | 739.90 |
| 2 | 746.20 | 753.50 | | | |
| 3 | 755.30 | 767.00 | 2 | 780.50 | 815.40 |
| 4 | 780.50 | 783.40 | | | |
| 5 | 786.00 | 797.00 | | | |
| 6 | 800.30 | 815.40 | 3 | 926.30 | 994.90 |
| 7 | 926.30 | 934.00 | | | |
| 8 | 960.40 | 970.70 | | | |
| 9 | 990.10 | 994.90 | 4 | 2109.90 | 2177.70 |
| 10 | 2109.90 | 2112.50 | | | |
| 11 | 2118.50 | 2120.50 | | | |
| 12 | 2153.50 | 2159.00 | | | |
| 13 | 2164.00 | 2170.00 | | | |
| 14 | 2174.00 | 2177.70 | 5 | 2187.90 | 2219.90 |
| 15 | 2187.90 | 2199.30 | | | |
| 16 | 2201.40 | 2204.20 | | | |
| 17 | 2206.10 | 2211.00 | | | |
| 18 | 2212.10 | 2219.90 | 6 | 2850.00 | 2972.00 |
| 19 | 2850.00 | 2892.00 | | | |
| 20 | 2895.30 | 2925.30 | | | |
| 21 | 2939.00 | 2945.00 | | | |
| 22 | 2949.60 | 2952.60 | | | |
| 23 | 2962.90 | 2965.00 | | | |
| 24 | 2970.30 | 2972.00 | 7 | 2860.00 | 2950.10 |
| 25 | 2860.00 | 2888.00 | | | |
| 26 | 2894.20 | 2898.00 | | | |
| 27 | 2904.90 | 2908.10 | | | |
| 28 | 2914.80 | 2928.60 | | | |
| 29 | 2936.40 | 2938.80 | | | |
| 30 | 2946.80 | 2950.10 | | | |

**Table B-6: Analysis Frequency ranges (note all regions are in wavenumbers). The components in region are defined as: S, where the primary standard is applied to the subject species; I where the component identified is a possible interferent to the subject species and – where the component is not a known interferent to the subject species investigated.**

| | | | Components in Regions | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $H_2O$ | $CO_2$ | CO | $N_2O$ | $CH_4$ | $NH_3$ | HCONT |
| # | Region Start | End | | | | | | | |
| 1 | 723.30 | 767.00 | I | S | - | - | - | - | - |
| 2 | 780.50 | 815.40 | S | - | - | - | - | - | - |
| 3 | 926.30 | 994.90 | I | I | - | - | - | S | - |
| 4 | 2109.90 | 2177.70 | I | I | S | - | - | - | - |
| 5 | 2187.90 | 2219.90 | I | I | I | S | - | - | - |
| 6 | 2850.00 | 2972.00 | I | - | - | - | I | - | S |
| 7 | 2860.00 | 2950.10 | I | - | - | - | S | - | I |

**Table B-7 Air Sampling Setup Data:**

| | |
|---|---|
| Sample heights: | 1 m, 2 m, 5m, 10 m, inside trailer |
| Sample line length | 100 ft, 100 ft, 100 ft, 100 ft, 0 ft |
| Nominal flow rate | 7.1 LPM |
| Cell flow rate | 7.6 LPM |
| Ambient flow rater | 6.7 LPM |
| Sample line transit | 8.6 sec |
| Cell residence time | 16 sec |

**Table B-8 FTIR Setup Data:**

| | |
|---|---|
| Resolution | 0.5 cm-1 |
| Wavenumber range: | 650 to 4000 5 cm-1 |
| Scans per sample: | 20 |
| Time per sample | ~30 sec |
| Path length | 8.28 m |
| Sample pressure | ~ 660 torr |
| Sample temperature | 35 oC |
| Sample cell volume | 2 liter |

**Table B-9 Sampling Time Periods**

1) Week of Oct 26, 2007
2) Week of Nov 2, 2007
3) Week of Nov 9, 2007
4)Week of Nov 16, 2007 (Note data taken 11/22 to 11/24 is included for completeness but not used in any calculations as the FTIR suffered a malfunction)
5) Nov 27-30, 2007
6) Week of Nov 30, 2007
7) Week of Dec 8 2007
8) Feb 8 – 9, 2007

**Table B-10 Data Plots for each Time Period**

1) Meteorological Data 1
2) Meteorological Data 3
3) H2O Concentration
4) CO2 Concentration
5) CO Concentration
6) N2O Concentration
7) CH4 Concentration
8) NH3 Concentration
9) Hydrocarbon Concentration
10) Total  N2O Flux at each elevation